F. .TENT COOPERATION TREA. /

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 19 April 2000 (19.04.00)	
International application No. PCT/US99/17422	**Applicant's or agent's file reference** 7024409PUR93
International filing date (day/month/year) 30 July 1999 (30.07.99)	**Priority date** (day/month/year) 30 July 1998 (30.07.98)
Applicant MANSOUR, Said et al	

1. The designated Office is hereby notified of its election made:

   ☒ in the demand filed with the International Preliminary Examining Authority on:

   29 February 2000 (29.02.00)

   ☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was ☐ was not

   made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer F. Baechler Telephone No.: (41-22) 338.83.38

REGARDING THE INTERNATIONAL APPLICATION OF
PURDUE RESEARCH FOUNDATION, etal.

DOCKET OR REFERENCE NUMBER
7024409PUR93

ENTITLED:
LOW TEMPERATURE OXYGEN GAS SENSOR

09/744793
528 Rec'd PCT/PTO 30 JAN 2001

Certification under 37 CFR 1.10 (if applicable)

EL016469525US
"Express Mail" mailing number

30 July 1999
Date of Deposit

I hereby certify that this application is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Commissioner of Patents and Trademarks, Washington, D.C. 20231.

Linda C. Shelby
(Typed or printed name of person mailing application)

Linda C. Shelby
(Signature of person mailing application)

To the United States Receiving Office (RO/US):

Accompanying this transmittal letter is the above-identified International application, including a completed Request form (PCT/RO/101). Please process the application according to the provisions of the Patent Cooperation Treaty.

The following requests are made of the RO/US:

1. [XX] PREPARATION AND TRANSMITTAL OF CERTIFIED COPY OF PRIORITY DOCUMENTS—Please prepare and transmit to the International Bureau a certified copy of the United States origin priority documents identified in Box VI of the Request form (37 CFR 1.451).

   To cover the cost of copy preparation and certification (37 CFR 1.19(a)(3) and (b)(1)),
   - [XX] a (check) (money order) in the amount of $30.00 included in fee is attached to this transmittal letter.
   - [ ] the RO/US is hereby authorized to charge the following deposit account no.: ______________.

2. [XX] CHOICE OF INTERNATIONAL SEARCHING AUTHORITY—It is requested that the International Search be performed by the following International Searching Authority:
   - [XX] United States Patent and Trademark Office (ISA/US)
   - [ ] European Patent Office (ISA/EP)

   The appropriate Search fee for the above-named Authority is indicated on the Fee Calculation Sheet (PCT/RO/101 Annex).

3. [XX] SUPPLEMENTAL SEARCH FEES (ONLY WHEN ISA/US CONDUCTS THE INTERNATIONAL SEARCH.)—Please charge any Supplemental Search fees that may be required by the United States International Searching Authority (ISA/US) to deposit account no.: 23-3030

   I understand that this authorization is subject to my oral confirmation thereof in each instance and that it in no way limits my right to submit a protest against payment of the Supplemental Search fees, but is merely an administrative aid to assure that the ISA/US may timely complete the Search Report.

NOTE: SUPPLEMENTAL SEARCH FEES FOR ISA/EP ARE PAYABLE DIRECTLY TO THE EUROPEAN PATENT OFFICE

4. [XX] DISCLOSURE INFORMATION—In order to assist in screening the accompanying International application for purposes of determining whether a license for foreign transmittal should and could be granted and for other purposes, the following information is supplied:

   A. [ ] There is no prior filed application relating to this invention.

   B. [XX] There is a prior application, serial number 60/094,721 filed on 30 July 1998 (30.07.98)
   60/123,819 11 March 1999 (11.03.99)
   which contains subject matter that is
   1. [X] substantially identical to that of the accompanying International application.
   2. [ ] less than that of the accompanying International application. The additional subject matter of the International application appears on pages(s) and line(s) ______________.
   3. [ ] more than that of the accompanying International application.

   C. [ ] Disclosure information cannot be covered by the language of Points 4A or 4B above due to the involvement of several prior applications or for other reasons. A separate sheet on which the disclosure information is explained is attached to this transmittal letter.

5. [XX] REQUEST FOR FOREIGN TRANSMITTAL LICENSE—According to the provisions of 35 U.S.C. 184 and 37 CFR 5.11, a license to transmit the accompanying International application to foreign agencies or international authorities is hereby requested.

SIGNER IS THE
- [ ] APPLICANT
- [ ] COMMON REPRESENTATIVE
- [X] (ATTORNEY) (AGENT)

REG NO #39,797

NAME OF SIGNER (typed)
L. Scott PAYNTER

SIGNATURE
L. Scott Paynter

PCT

FEE CALCULATION SHEET
Annex t the Request

For receiving Office use only

International application No.

Date stamp of the receiving Office

Applicant's or agent's file reference 7024409PUR93

Applicant
PURDUE RESEARCH FOUNDATION, etal.

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE . . . . 240 T

2. SEARCH FEE . . . . 700 S

International search to be carried out by US

(If two or more International Searching Authorities are competent in relation to the international application, indicate the name of the Authority which is chosen to carry out the international search.)

3. INTERNATIONAL FEE

Basic Fee

The international application contains 43 sheets.

first 30 sheets 455 b1

13 remaining sheets x 10 additional amount = 130 b2

Add amounts entered at b1 and b2 and enter total at B . . . . . 585 B

Designation Fees

The international application contains 79 designations.

10 number of designation fees payable *(maximum 10)* x 105 amount of designation fee = max. 1050 D

Add amounts entered at B and D and enter total at I . . . . 1635.00 I

(Applicants from certain States are entitled to a reduction of 75% of the international fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at I is 25% of the sum of the amounts entered at B and D.)

4. FEE FOR PRIORITY DOCUMENT *(if applicable)* . . . . 30 P

5. TOTAL FEES PAYABLE . . . . 2605.00 TOTAL

Add amounts entered at T, S, I and P, and enter total in the TOTAL box

☐ The designation fees are not paid at this time.

MODE OF PAYMENT

- [XX] authorization to charge deposit account (see below)
- [XX] cheque
- ☐ postal money order
- ☐ bank draft
- ☐ cash
- ☐ revenue stamps
- ☐ coupons
- ☐ other *(specify)*:

DEPOSIT ACCOUNT AUTHORIZATION *(this mode of payment may not be available at all receiving Offices)*

The RO/ US

☐ is hereby authorized to charge the total fees indicated above to my deposit account.

[XX] *(this check-box may be marked only if the conditions for deposit accounts of the receiving Office so permit)* is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.

☐ is hereby authorized to charge the fee for preparation and transmittal of the priority document to the International Bureau of WIPO to my deposit account.

Deposit Account No.	Date *(day/month/year)*	Signature
23-3030	30 July 1999	L. Scott PAYNTER, #39,797

PCT

For receiving Office use only
International Application No.
International Filing Date
Name of receiving Office and "PCT International Application"

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

Applicant's or agent's file reference (*if desired*) (*12 characters maximum*) 7024409PUR93

Box No. I TITLE OF INVENTION

LOW TEMPERATURE OXYGEN GAS SENSOR

Box No. II APPLICANT

Name and address: (*Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.*)

PURDUE RESEARCH FOUNDATION
Office of Technology Transfer
1063 Hovde Hall
West Lafayette, Indiana 47907 US

☐ This person is also inventor.

Telephone No. -

Facsimile No.

Teleprinter No.

State (*that is, country*) of nationality: US

State (*that is, country*) of residence: US

This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (*Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.*)

MANSOUR, Said
2818 Cambridge Street
West Lafayette, Indiana 47906
United States of America

This person is:
☐ applicant only
☒ applicant and inventor
☐ inventor only (*If this check-box is marked, do not fill in below.*)

State (*that is, country*) of nationality: US

State (*that is, country*) of residence: US

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative

Name and address: (*Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.*)

PAYNTER, L. Scott
WOODARD, EMHARDT, NAUGHTON, MORIARTY & MCNETT
Bank One Center/Tower, Suite 3700
111 Monument Circle
Indianapolis, Indiana 46204 US

Telephone No. 317-634-3456

Facsimile No. 317-637-7561

Teleprinter No. 810-341-3283

SEE CONTINUATION TO BOX NO. IV ON SHEET NO. 4

☐ **Address for correspondence:** Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

C ntinuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not be included in the request.

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

BRAZIER, Mark
3037 Courthouse Dr. #1
West Lafayette, Indiana 47906
United States of America

This person is:

- [ ] applicant only
- [X] applicant and inventor
- [ ] inventor only *(If this check-box is marked, do not fill in below.)*

State *(that is, country)* of nationality: US

State *(that is, country)* of residence: US

This person is applicant for the purposes of:

- [ ] all designated States
- [ ] all designated States except the United States of America
- [XX] the United States of America only
- [ ] the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

McELFRESH, Michael
931 Princess Drive
West Lafayette, Indiana 47906
United States of America

This person is:

- [ ] applicant only
- [XX] applicant and inventor
- [ ] inventor only *(If this check-box is marked, do not fill in below.)*

State *(that is, country)* of nationality: US

State *(that is, country)* of residence: US

This person is applicant for the purposes of:

- [ ] all designated States
- [ ] all designated States except the United States of America
- [XX] the United States of America only
- [ ] the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

This person is:

- [ ] applicant only
- [ ] applicant and inventor
- [ ] inventor only *(If this check-box is marked, do not fill in below.)*

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

This person is applicant for the purposes of:

- [ ] all designated States
- [ ] all designated States except the United States of America
- [ ] the United States of America only
- [ ] the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

This person is:

- [ ] applicant only
- [ ] applicant and inventor
- [ ] inventor only *(If this check-box is marked, do not fill in below.)*

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

This person is applicant for the purposes of:

- [ ] all designated States
- [ ] all designated States except the United States of America
- [ ] the United States of America only
- [ ] the States indicated in the Supplemental Box

- [ ] Further applicants and/or (further) inventors are indicated on another continuation sheet.

B x No.V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) *(mark the applicable check-boxes: at least one must be marked)*:

Regional Patent

☒ AP ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT

☒ EA Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT

☒ EP European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT

☒ OA OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT *(if other kind of protection or treatment desired, specify on dotted line)* ....

National Patent *(if other kind of protection or treatment desired, specify on dotted line)*:

☒ AL Albania ....
☒ AM Armenia ....
☒ AT Austria ....
☒ AU Australia ....
☒ AZ Azerbaijan
☒ BA Bosnia and Herzegovina ....
☒ BB Barbados
☒ BG Bulgaria ....
☒ BR Brazil ....
☒ BY Belarus ....
☒ CA Canada
☒ CH and LI Switzerland and Liechtenstein
☒ CN China ....
☒ CU Cuba ....
☒ CZ Czech Republic ....
☒ DE Germany ....
☒ DK Denmark ....
☒ EE Estonia ....
☒ ES Spain ....
☒ FI Finland ....
☒ GB United Kingdom
☒ GD Grenada
☒ GE Georgia ....
☒ GH Ghana ....
☒ GM Gambia
☒ HR Croatia ....
☒ HU Hungary ....
☒ ID Indonesia
☒ IL Israel ....
☒ IN India ....
☒ IS Iceland
☒ JP Japan ....
☒ KE Kenya ....
☒ KG Kyrgyzstan ....
☒ KP Democratic People's Republic of Korea ....
☒ KR Republic of Korea ....
☒ KZ Kazakhstan ....
☒ LC Saint Lucia
☒ LK Sri Lanka
☒ LR Liberia
☒ LS Lesotho ....
☒ LT Lithuania
☒ LU Luxembourg
☒ LV Latvia
☒ MD Republic of Moldova ....
☒ MG Madagascar ....
☒ MK The former Yugoslav Republic of Macedonia ....
☒ MN Mongolia
☒ MW Malawi ....
☒ MX Mexico ....
☒ NO Norway
☒ NZ New Zealand ....
☒ PL Poland ....
☒ PT Portugal ....
☒ RO Romania
☒ RU Russian Federation ....
☒ SD Sudan
☒ SE Sweden
☒ SG Singapore
☒ SI Slovenia ....
☒ SK Slovakia ....
☒ SL Sierra Leone
☒ TJ Tajikistan ....
☒ TM Turkmenistan ....
☒ TR Turkey ....
☒ TT Trinidad and Tobago ....
☒ UA Ukraine ....
☒ UG Uganda ....
☒ US United States of America ....
☒ UZ Uzbekistan ....
☒ VN Viet Nam ....
☒ YU Yugoslavia ....
☒ ZW Zimbabwe ....

Check-boxes reserved for designating States (for the purposes of a national patent) which have become party to the PCT after issuance of this sheet:

☒ AE - United Arab Emirates
☒ ZA - South Africa
☐ ....

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. *(Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)*

Supplemental Box *If the Supplemental Box is not used, this sheet should not be included in the request.*

1. If, in any of the Boxes, ***the space is insufficient*** *to furnish all the information: in such case, write "Continuation of Box No. ..." [indicate the number of the Box] and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:*

(i) ***if more than two persons are involved as applicants and/or inventors*** *and no "continuation sheet" is available: in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;*

(ii) if, in Box No. II or in any of the sub-boxes of Box No. III, the indication ***"the States indicated in the Supplemental Box"*** *is checked: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;*

(iii) if, in Box No. II or in any of the sub-boxes of Box No. III, ***the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America****: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;*

(iv) if, in addition to the agent(s) indicated in Box No. IV, there are ***further agents****: in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box No. IV;*

(v) if, in Box No. V, the name of any State (or OAPI) is accompanied by the indication ***"patent of addition,"*** *or* ***"certificate of addition,"*** *or if, in Box No. V, the name of the United States of America is accompanied by an indication* ***"continuation"*** *or* ***"continuation-in-part"****: in such case, write "Continuation of Box No. V" and the name of each State involved (or OAPI), and after the name of each such State (or OAPI), the number of the parent title or parent application and the date of grant of the parent title or filing of the parent application;*

(vi) if, in Box No. VI, there are ***more than three earlier applications whose priority is claimed****: in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI;*

(vii) if, in Box No. VI, ***the earlier application is an ARIPO application****: in such case, write "Continuation of Box No. VI", specify the number of the item corresponding to that earlier application and indicate at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed.*

2. If, with regard to the ***precautionary designation statement*** *contained in Box No. V, the applicant wishes to exclude any State(s) from the scope of that statement: in such case, write "Designation(s) excluded from precautionary designation statement" and indicate the name or two-letter code of each State so excluded.*

3. If the applicant claims, in respect of any designated Office, the benefits of provisions of the national law concerning ***non-prejudicial disclosures or exceptions to lack of novelty****: in such case, write "Statement concerning non-prejudicial disclosures or exceptions to lack of novelty" and furnish that statement below.*

Continuation to Box No. IV Agent

WOODARD, Harold R.; EMHARDT, C. David; NAUGHTON, Joseph A., Jr.; MORIARTY, John V.; McNETT, John C.; HENRY, Thomas Q.; DURLACHER, James M.; REEVES, Charles R.; WAGNER, Vincent O.; ZLATOS, Steve; BEREVESKOS, Spiro; BAHRET, William F.; BROWNING, Clifford W.; FRISK, R. Randall; LUEDERS, Daniel J.; GANDY, Kenneth A.; THOMAS, Timothy N.; SISSELMAN, Kerry P.; JONES, Kurt N.; ALLIE, John H.; BANTA, Holiday W.; COLE, Troy J.; PAYNTER, L. Scott; LOWES, J. Andrew; MEYER, Charles J.; HARRIS, Darrin Wesley; SCHANTZ, Matthew R.; COY, Gregory B.; HIDAY, Lisa A.; DANILUCK, John V.; BROWN, Christopher A.;SCHWARTZ, Jason J.; USHER, Arthur J. IV; COLLIER, Douglas A.; MYERS, James B. Jr.; STEVENS, Scott J., and ROWE, James L., all of Woodard, Emhardt, Naughton, Moriarty & McNett, Bank One Center/Tower, Suite 3700, 111 Monument Circle, Indianapolis, Indiana 46204 United States of America

B x N . VI PRIORITY CLAI. ☐ Further priority clai... ...re indicated in the Supplemental Box.

Filing date of earlier application *(day/month/year)*	Number of earlier application	Where earlier application is: national application: country	regi nal application:* regional Office	international application: receiving Office
item (1) (30.07.98) 30 July 1998	60/094,721	US		
item (2)(11.03.99) 11 March 1999	60/123,819	US		
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) *(only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office)* identified above as item(s): (1), (2)

** Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.*

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) *(if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):*

ISA / US

Request to use results of earlier search; reference to that search *(if an earlier search has been carried out by or requested from the International Searching Authority):*

Date *(day/month/year)*	Number	Country *(or regional Office)*
30 July 1998 (30.07.98)	60/094,721	US
11 March 1999 (11.03.99)	60/123,819	US

Box No. VIII CHECK LIST; LANGUAGE OF FILING

This international application contains the following number of sheets:

request	:	5
description (excluding sequence listing part)	:	19
claims	:	7
abstract	:	1
drawings	:	11
sequence listing part of description	:	—
Total number of sheets	:	43

This international application is accompanied by the item(s) marked below:

1. ☒ fee calculation sheet
2. ☐ separate signed power of attorney
3. ☐ copy of general power of attorney; reference number, if any:
4. ☐ statement explaining lack of signature
5. ☐ priority document(s) identified in Box No. VI as item(s):
6. ☐ translation of international application into (language):
7. ☐ separate indications concerning deposited microorganism or other biological material
8. ☐ nucleotide and/or amino acid sequence listing in computer readable form
9. ☒ other *(specify)*: Transmittal Letter (dup)

Figure of the drawings which should accompany the abstract: 3

Language of filing of the international application: English

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

Applicant(s):

PURDUE RESEARCH FOUNDATION
MANSOUR, Said
BRAZIER, Mark
MCELFRESH, Michael

Agent:

L Scott Paynter

(L. Scott PAYNTER)

For receiving Office use only

1. Date of actual receipt of the purported international application:	2. Drawings:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	☐ received:
4. Date of timely receipt of the required corrections under PCT Article 11(2):	☐ not received:
5. International Searching Authority (if two or more are competent): ISA /	6. ☐ Transmittal of search copy delayed until search fee is paid.

For International Bureau use only

Date of receipt of the record copy by the International Bureau:

09/744179

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

JC02 Rec'd PCT/PTO 30 JAN 2001

In re PCT application of PURDUE RESEARCH FOUNDATION, et al.	)
International Application Number PCT/US99/17422	) Mailing Date 08 March 2000
International Filing Date 30 July 1999	) Agent's File Reference: 7024409PUR93
Title of Invention LOW TEMPERATURE OXYGEN GAS SENSOR	)

AMENDMENT UNDER ARTICLE 34

Assistant Commissioner for Patents
Box PCT
Washington, D.C. 20231

ATTN: IPEA/US

"Express Mail" label number EM 548483 354 US
Date of Deposit 13 March 2000
I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR §1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

Signature of person mailing paper or fee

Dear Sir/Madam:

Pursuant to Article 34 of the Patent Cooperation Treaty (PCT), Applicant hereby makes the following amendments to the claims as filed in the above-identified application. Substitute sheets 20-26 are submitted herewith to change the claims.

REMARKS

Claim 1 has been amended to recite that the oxygen sensor includes a ferroelectric metal oxide sensor. A new claim has been added as claim 2. The original claim 7 has been cancelled. Original claims 2-6 have been renumbered as claims 3-7, respectively. The original claim 10 has been renumbered as claim 11, and the original claim 11 has been renumbered as claim 10 to provide antecedent basis for the terms "x" and "y". Numbering of claims 8-9, and 12-53 remains the same. The preambles of claims 3-11, 13-15, 17, 21, 23, 25, 26, 30, 32, 34, 35, 38, 40, 41, 43, 44, and 51-53 have been amended to change dependency, removing stacked multiple dependent claims. Applicant respectfully requests that the present Amendment be entered in the present application, and that further actions be taken on the application.

Respectfully submitted

By *[signature]*

James B. Myers, #42,021
Woodard, Emhardt, Naughton,
Moriarty & McNett
Bank One Center/Tower, Suite 3700
111 Monument Circle
Indianapolis, Indiana 46204 US
(317) 634-3456

80211
Enclosure: Article 34 Amendment

CLAIMS

What is claimed is:

1. An apparatus comprising an oxygen sensor including a ferroelectric metal oxide sensing member having an effective operating temperature below about 400K.

2. An apparatus comprising an oxygen sensor including a non-stoichiometric metal oxide sensing member having at least two compositional constituents in a ratio that increases along a predetermined direction through said sensing member to provide a corresponding compositional gradient, said non-stoichiometric metal oxide having an effective operating temperature below about 400K.

3. The apparatus of claim 1 or 2 having an effective operating temperature below about 375K.

4. The apparatus of claim 1 or 2 having an effective operating temperature below about 300K.

5. The apparatus of claim 1 or 2, wherein said sensor includes at least two metallic electrodes.

6. The apparatus of claim 5, wherein said electrodes are formed from a material selected from platinum, silver, gold, metal phthalocyanine, and conductive metal oxide.

7. The apparatus of claim 1 or 2 and further comprising a circuit electrically coupled to said sensing member operable to apply a time varying electric field to said sensing member.

8. The apparatus of claim 2, wherein said at least two compositional constituents are zirconia and titania.

9. The apparatus of claim 2 or 8, wherein said gradient is established by a number of differently composed layers.

10. The apparatus of any of claims 1 or 2, wherein said sensing member is formed of $PbZr_xTi_yO_3$; where x is in a range of about 0.5 to about 0.8 and y is in a range of about 0.2 to about 0.5.

11. The apparatus of claim 10, wherein x increases along a direction through said sensing member and y decreases along said direction.

12. The apparatus of claim 11, wherein x is in a range of about 0.55 to about 0.75 and y is in a range of about 0.25 to about 0.45.

13. The apparatus of claim 10, wherein said sensing member includes a number of layers each having a different ratio of x to y.

14. The apparatus of claim 10, wherein x is about 0.55 and y is about 0.45 along a first surface of said sensing member and x is about 0.75 and y is about 0.25 along a second surface of said sensing member opposite said first surface.

15. The apparatus of claim 1 or 2, wherein said sensing member is comprised of an oxygen deficient ionic oxide material.

16. The apparatus of claim 15 wherein the said sensing member is comprised of a YSZ material.

17. A method of use, comprising detecting oxygen in an intake or exhaust stream of a vehicle with the apparatus of claim 1 or 2.

18. A method of manufacture, comprising:

providing a source of ferroelectric material having a first region with a first composition and a second region with a second composition different from the first composition;

irradiating a portion of the first region and a portion of the second region with a laser to release a mixture from the source with a predetermined ratio of the first composition to the second composition; and

forming a layer of a sensing matrix from the mixture, the mixture corresponding to the ratio.

19. The method of claim 18, wherein said source is a solid composed of $PbZr_xTi_yO_3$; where x and y have a first predetermined ratio in the first region and a second predetermined ratio in the second region, the first predetermined ratio being different from the second predetermined ratio.

20. The method of claim 19, wherein x is about 0.75 in the first region and about 0.55 in the second region and y is about 0.25 in the first region and about 0.45 in the second region.

21. The method of claim 18, wherein the first region is adjacent the second region with an interface oriented at a predetermined position relative to the laser.

22. The method of any of claims 18-21 further comprising performing said irradiating of a number of different portions of the first and second regions to form a graded ferroelectric sensing member.

23. The method of any of claims 18-21, wherein said irradiating includes scanning a predetermined path along the source with the laser.

24. The method of claim 23, wherein said path includes a number of segments each corresponding to a different ratio of the first composition to the second composition.

25. The method of any of claims 18-21, wherein said forming includes depositing the mixture on a substrate.

26. An oxygen sensor formed by the method of any of claims 18-21.

27. A method of manufacture, comprising:

providing a source of ferroelectric material having a first region with a first composition and a second region with a second composition different from the first composition;

generating a number of plumes each having a different ratio of the first composition to the second composition, each of the plumes being formed from different areas of the first and second regions; and

forming a number of layers each corresponding to a different one of the plumes, the layers each having the different ratio of the first composition to the second composition to provide a ferroelectric device with a predetermined compositional gradient.

28. The method of claim 27, wherein the source is a solid composed of $PbZr_xTi_yO_3$; where x and y have a first predetermined ratio in the first region and a second predetermined ratio in the second region, the first predetermined ratio being different from the second predetermined ratio.

29. The method of claim 28, wherein x is about 0.75 in the first region and about 0.55 in the second region and y is about 0.25 in the first region and about 0.45 in the second region.

30. The method of claim 27, wherein the first region is adjacent the second region with an interface oriented at a predetermined position relative to a device for performing said generating.

31. The method of any of claims 27-30, wherein said generating the plumes includes irradiating a corresponding number of different portions of the first and second regions.

32. The method of any of claims 27-30, wherein said irradiating includes scanning across a predetermined path along the source with a laser.

33. The method of claim 32, wherein said path includes a number of segments each corresponding to a different one of the plumes.

34. The method of any of claims 27-30, wherein said forming includes depositing material from a first one of the plumes on a substrate.

35. An oxygen sensor formed by the method of any of claims 27-30.

36. An apparatus comprising an oxygen sensor including a PZT ferroelectric sensing member.

37. The apparatus of claim 36 wherein said sensing member is comprised of a graded ferroelectric material.

38. The apparatus of claim 36 wherein the said sensor includes at least two metallic electrodes.

39. The apparatus of claim 38 wherein said electrodes are formed from a material selected from platinum, silver, gold, metal phthalocyanine, and conductive metal oxide.

40. The apparatus of claim 36 and further comprising a circuit electrically coupled to said sensing member operable to apply a time varying electric field to said sensing member.

41. The apparatus of any of claims 36-40, wherein a ratio between two compositional constituents increases along a predetermined direction through said sensing member to provide a corresponding compositional gradient.

42. The apparatus of claim 41, wherein said gradient is established by a number of differently composed layers.

43. The apparatus of claim 41 or 42, wherein said two compositional constituents are zirconia and titania.

44. The apparatus of any of claims 36-40 wherein said sensing member is formed of $PbZr_xTi_yO_3$; wherein x is in a range of about 0.5 to about 0.8 and y is in a range of about 0.2 to about 0.5.

45. The apparatus of claim 44 wherein x is in a range of about 0.55 to about 0.75 and y is in a range of about 0.25 to about 0.45.

46. A method of use, comprising detecting oxygen in an intake or exhaust stream of a vehicle with the apparatus of any of claims 36-40.

47. A combination, comprising:

a nonstoichiometric metal oxide sensing member to detect oxygen; and

a circuit electrically coupled to said sensing member operable to apply a time varying electric field to said sensing member having a peak magnitude of at least about 1 volt per μm.

48. A combination, comprising:

providing a nonstoichiometric metal oxide sensing member;

applying a time varying electric field to said sensing member having a peak magnitude of at least about 1 volt per μm; and

sensing oxygen with said sensing member during said applying.

49. The combination of claim 47 or 48, wherein said peak magnitude is in a range of about 1 volt per μm to about 1000 volts per μm.

50. The combination of claim 49, wherein said peak magnitude is in a range of about 10 volts per μm to about 100 volts per μm.

51. The combination of claim 47 or 48 wherein said sensing member is comprised of a ferroelectric material.

52. The combination of claim 47 or 48, wherein said sensing member is comprised of a PZT material.

53. The combination of claim 47 or 48, wherein the system is operable to detect oxygen concentration at a temperature below about 400K.

PATENT COOPERATION TREATY 09/744479 RECEIVED

NOV 21 2000

Woodard, Emhardt, Naughton Moriarty & McNett

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To: L. SCOTT PAYNTER
WOODWARD, EMHARDT, NAUGHTON, MORIARTY & MCNETT
BANK ONE CENTER/TOWER, SUITE 3700
111 MONUMENT CIRCLE
INDIANAPOLIS, INDIANA 46204

PCT

WRITTEN OPINION

(PCT Rule 66)

Date of Mailing *(day/month/year)*	14 NOV 2000
Applicant's or agent's file reference 7024409PUR93	**REPLY DUE** within **ONE** months from the above date of mailing

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US99/17422	30 JULY 1999	30 JULY 1998

International Patent Classification (IPC) or both national classification and IPC
Please See Supplemental Sheet.

Applicant
PERDUE RESEARCH FOUNDATION

ENTERED
12-14-00

1. This written opinion is the second (first, etc.) drawn by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

- I [X] Basis of the opinion
- II [ ] Priority
- III [X] Non-establishment of opinion with regard to novelty, inventive step or industrial applicability
- IV [X] Lack of unity of invention
- V [X] Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI [ ] Certain documents cited
- VII [ ] Certain defects in the international application
- VIII [X] Certain observations on the international application

3. The applicant is hereby invited to reply to this opinion.

When? See the time limit indicated above. ~~The applicant may, before the expiration of that time limit, request this Authority to grant an extension., see Rule 66.2(d).~~

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also For an additional opportunity to submit amendments, see Rule 66.4.
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 *bis*.
For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 30 NOVEMBER 2000.

Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer ARLEN SODERQUIST DEBORAH THOMAS PARALEGAL SPECIALIST
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0661

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To: L. SCOTT PAYNTER
WOODWARD, EMHARDT, NAUGHTON, MORIARTY & MCNETT
BANK ONE CENTER/TOWER, SUITE 3700
111 MONUMENT CIRCLE
INDIANAPOLIS, INDIANA 46204

PCT

WRITTEN OPINION

(PCT Rule 66)

Date of Mailing *(day/month/year)*	14 NOV 2000
Applicant's or agent's file reference: 7024409PUR93	**REPLY DUE** within ONE months from the above date of mailing

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US99/17422	30 JULY 1999	30 JULY 1998

International Patent Classification (IPC) or both national classification and IPC
Please See Supplemental Sheet.

Applicant
PERDUE RESEARCH FOUNDATION

1. This written opinion is the second (first, etc.) drawn by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

   - I [X] Basis of the opinion
   - II [ ] Priority
   - III [X] Non-establishment of opinion with regard to novelty, inventive step or industrial applicability
   - IV [X] Lack of unity of invention
   - V [X] Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI [ ] Certain documents cited
   - VII [ ] Certain defects in the international application
   - VIII [X] Certain observations on the international application

3. The applicant is hereby invited to reply to this opinion.

   When? See the time limit indicated above. ~~The applicant may, before the expiration of that time limit, request this Authority to grant an extension., see Rule 66.2(d).~~

   How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

   Also For an additional opportunity to submit amendments, see Rule 66.4.
   For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 *bis*.
   For an informal communication with the examiner, see Rule 66.6.

   If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 30 NOVEMBER 2000.

Name and mailing address of the IPEA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	ARLEN SODERQUIST DEBORAH THOMAS PARALEGAL SPECIALIST
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0661

WRITTEN OPINION

International application No.
PCT/US99/17422

I. Basis f the opinion

1. With regard to the elements of the international application:*

- [ ] the international application as originally filed
- [X] the description:
  pages (See Attached), as originally filed
  pages ______, filed with the demand
  pages ______, filed with the letter of ______
- [X] the claims:
  pages (See Attached), as originally filed
  pages ______, as amended (together with any statement) under Article 19
  pages ______, filed with the demand
  pages ______, filed with the letter of ______
- [X] the drawings:
  pages (See Attached), as originally filed
  pages ______, filed with the demand
  pages ______, filed with the letter of ______
- [X] the sequence listing part of the description:
  pages (See Attached), as originally filed
  pages ______, filed with the demand
  pages ______, filed with the letter of ______

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language ______ which is:

- [ ] the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- [ ] the language of publication of the international application (under Rule 48.3(b)).
- [ ] the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the written opinion was drawn on the basis of the sequence listing:

- [ ] contained in the international application in printed form.
- [ ] filed together with the international application in computer readable form.
- [ ] furnished subsequently to this Authority in written form.
- [ ] furnished subsequently to this Authority in computer readable form.
- [ ] The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- [ ] The statement that the information recorded in computer readable form is identical to the writen sequence listing has been furnished.

4. [X] The amendments have resulted in the cancellation of:
   - [X] the description, pages NONE
   - [X] the claims, Nos. NONE
   - [X] the drawings, sheets/~~fig~~ NONE

5. [ ] This opinion has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

* *Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed".*

WRITTEN OPINION

International application No.
PCT/US99/17422

III. N n-establishment f pinion with regard to n velty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non obvious), or to be industrially applicable have not been and will not be examined in respect of:

☐ the entire international application.

☒ claims Nos. 43

because:

☐ the said international application, or the said claim Nos. _ relate to the following subject matter which does not require international preliminary examination *(specify)*.

☒ the description, claims or drawings *(indicate particular elements below)* or said claims Nos. 43 are so unclear that no meaningful opinion could be formed *(specify)*.

Claim 43 is an imporper multiple dependent claim.

☐ the claims, or said claims Nos. _ are so inadequately supported by the description that no meaningful opinion could be formed.

☐ no international search report has been established for said claims Nos. _.

2. A written opinion cannot be drawn due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

☐ the written form has not been furnished or does not comply with the standard.

☐ the computer readable form has not been furnished or does not comply with the standard.

WRITTEN OPINION

International application No.
PCT/US99/17422

IV. Lack f unity f inventi n

1. In response to the invitation (Form PCT/IPEA/405) to restrict or pay additional fees the applicant has:

- [ ] restricted the claims. (See Supplemental Sheet)
- [x] paid additional fees.
- [ ] paid additional fees under protest.
- [ ] neither restricted nor paid additional fees.

2. This Authority found that the requirement of unity of invention is not complied with for the following reasons and chose, according to Rule 68.1 not to invite the applicant to restrict or pay additional fees:

3. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this opinion:

- [ ] all parts.
- [x] the parts relating to claims Nos. 1-42 and 44-53.

WRITTEN OPINION

International application No.
PCT/US99/17422

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. statement

Novelty (N)	Claims	2,7-14,17-42,44-53	YES
	Claims	1,3-7,15-16	NO
Inventive Step (IS)	Claims	18-35	YES
	Claims	1-17,36-42,44-53	NO
Industrial Applicability (IA)	Claims	1-42,44-53	YES
	Claims	NONE	NO

2. citations and explanations

(See Supplemental Sheet.)

VIII. Certain observati ns on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claims 26 and 35 are objected to under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 6 because the claims are indefinite for the following reason(s): they do not have sufficient structure to allow them to function as a sensor.

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

TIME LIMIT:

The time limit set for response to a Written Opinion may not be extended. 37 CFR 1.484(d). Any response received after the expiration of the time limit set in the Written Opinion will not be considered in preparing the International Preliminary Examination Report.

CLASSIFICATION:

The International Patent Classification (IPC) and/or the National classification are as listed below:
IPC(7): G01N 27/00, 33/00 and US Cl.: 73/23.31, 23.32; 422/88, 90, 94, 98; 436/127, 136, 137, 138, 151

I. BASIS OF OPINION:

This opinion has been drawn on the basis of the description:
page(s) 1-19, as originally filed.
page(s) NONE, filed with the demand.
and additional amendments:
NONE

This opinion has been drawn on the basis of the claims:
page(s) NONE, as originally filed.
page(s) NONE, as amended under Article 19.
page(s) NONE, filed with the demand.
and additional amendments:
Pages 20-26, filed with the letter of 13 March 2000.

This opinion has been drawn on the basis of the drawings:
page(s) 1-11, as originally filed.
page(s) NONE, filed with the demand.
and additional amendments:
NONE

This opinion has been drawn on the basis of the sequence listing part of the description:
page(s) NONE, as originally filed.
pages(s) NONE, filed with the demand.
and additional amendments:
NONE

IV. LACK OF UNITY OF INVENTION:

1. This response is made to a telephone Lack of Unity requirement (see telephone memorandum attached hereto or attached to a prior Written Opinion).

V. 2. REASONED STATEMENTS - CITATIONS AND EXPLANATIONS (Continued):

Claims 1, 3-7(as they depend from claim 1) and 15-16 lack novelty under PCT Article 33(2) as being anticipated by Miyahara et al. In the paper Miyahara teaches a field-effect transistor using a solid electrolyte as a new oxygen sensor. A field-effect transistor (FET) using a solid electrolyte is proposed as a new oxygen sensor. The sensor is fabricated by depositing a thin layer of yttria-stabilized zirconia (YSZ) on a gate insulator of an insulated gate field-effect transistor (IGFET). As an IGFET has an ability to transform impedance, the potential change produced at the interface between the YSZ layer and a platinum gate electrode can be detected stably, even if the impedance of the YSZ is very high. The response of the fabricated sensor

Supplemental B x
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

showed good reproducibility at 20°. A linear relation between output voltage and logarithmic partial pressure of oxygen was obtained in the range 0.01-1 atmospheres. Sensitivity of the sensor depends on the thickness of the Pt-gate electrode and sputtering conditions of the YSZ layer. Although selectivity to hydrogen and carbon monoxide was not good at room temperature, it could be improved by increasing the operating temperature to 100°. The developed sensor has several advantages including small size, low output impedance, and solid-state construction. It is potentially applicable to medical uses, process control, and automobiles.

Claims 2, 3-7 (as they depend from claim 2), 8-14, 17, 36-42 and 44-53 lack an inventive step under PCT Article 33(3) as being obvious over the prior art as applied in the immediately preceding paragraph and further in view of Vetrone et al, Murayama et al. and Cattan et al. Miyahara does not teach other types of materials or specifics related to the structure of the material.

In the abstract Vetrone et al. discusses the significance of microstructure for MOCVD-grown YSZ thin film gas sensor. They report the fabrication and characterization of a low temperature (200°-400°) thin film gas sensor constructed from a MOCVD-grown yttria-stabilized zirconia (YSZ) layer sandwiched between two platinum thin film electrodes. A reproducible gas-sensing response is produced by applying a cyclic voltage which generates voltammograms with gas-specific current peaks and shapes. Growth conditions are optimized for preparing YSZ films having dense microstructures, low leakage currents, and maximum ion conductivities. In particular, the effect of growth temperature on film morphology and texture is discussed and related to the electrical and gas-sensing properties of the thin film sensor device.

In the abstract Murayama et al teach a breath detection sensor for oxygen delivery system. An inspiration and expiration detection sensor has been developed from remodeling of the air pressure sensor. The sensor element is pyroelectric PZT, which detects temperature change and derives the pressure signal. Air of the breath, therefore, must flow through a heater which is set in front of the sensor element. The device shows remarkably high sensitivity and high reliability. It has been applied to the oxygen delivery system for the dyspneal patient.

In the abstract Cattan et al. discusses the properties of a PZT material. The specific material listed is $Pb(Zr_{0.55}, Ti_{0.45})O_3$.

It would have been obvious to one of skill in the art to optimize the properties of the Miyahara et al. device according to the teachings of Vetrone et al. because of the ability to control sensor properties as taught by Vetrone et al. It also would have been obvious to use other materials such as the PZT material of Murayama et al. which Cattan et al. shows has the claimed structure in the Miyahara et al. device because of their known sensitivity to oxygen.

Claims 18-35 the criteria set out in PCT Article 33(2)-(4), because the prior art does not teach or fairly suggest the methods of manufacture as claimed with the use of a ferroelectric material with two regions of different composition which are volatilized by irradiating with a laser to form a sensing matrix based on the ratio of the first composition to the second composition in the released materials.

Supplemental B x
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 12

-------------------- NEW CITATIONS --------------------

NONE

CHAPTER II
PCT TELEPHONE MEMORANDUM
FOR
LACK OF UNITY OF INVENTION

PCT No.: PCT/US99/17422
Examiner: ARLEN SODERQUIST
Person spoken to: L. Scott Paynter
Date of call: 24 MAY 2000

☒ Amount of payment approved: $280.00

☒ Deposit account number to be charged: 23-3030

☒ Applicant elected to pay for ALL additional inventions

☐ Applicant elected to pay only for the additional inventions covered by

☐ Group(s):

-- encompassing --

☐ Claim(s):

☐ Applicant elected a single invention, but elected NOT to pay for any additional inventions. Therefore, Group _, encompassing Claim(s) _, defining the single invention elected by the Applicant, has been examined.

☒ Applicant was orally advised that there is no right to protest for any group not paid for.

☒ Applicant was orally advised that any protest must be filed no later than 1 Month from the mailing of the Opinion (Form PCT/IPEA/408) or the Final Report (Form PCT/IPEA/409).

Time Limit For Filing A Protest

Applicant is hereby given 1 Month from the mailing date of this Opinion/Final Report in which to file a protest of the holding of lack of unity of invention. In accordance with PCT Rule 68.3, applicant may protest the holding of lack of unity only with respect to the group(s) paid for.

Detailed Reasons For Holding Lack of Unity Of Invention:

(Continued on a separate sheet)

Note: A copy of this form must be attached to the Opinion/Final Report.

ATTACHMENT TO CHAPTER II PCT TELEPHONE MEMORANDUM FOR LACK OF UNITY OF INVENTION

Itemized Summary Of Claim Groupings:
This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-6, 15, 16, and 47-50, drawn to apparatus and method including a nonstoichiometric metal oxide sensing member having an effective operating temperature below 400K.
Group II, claim(s) 18-21 and 27-30, drawn to a method of manufacture and an oxygen sensor including a ferroelectric member.
Group III, claim(s) 36-39 and 41-43, drawn to an oxygen sensor and its method of use in which the sensor includes a PZT ferroelectric sensing member.

Detailed Reasons For Holding Lack Of Unity Of Invention:
The inventions listed as Groups I and II or III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: there is no clear connection between the nonstoichiometric sensing material of Group I and the ferroelectric sensing material of either Groups II or III. The sensing materials of Group I while possibly including ferroelectric materials are not so limited. Conversely the sensing materials of Groups II and III also possibly contain nonstoichiometric materials, but are not limited thereto. Additionally Group I has an effective operating temperature limitation that is not found in either of Groups II or III.

The inventions listed as Groups II and III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the sensing material formed through the process of Group II is required to be a mixture of two ferroelectric materials while the ferroelectric sensing material of Group III is limited to a certain type of ferroelectric material. There is no indication that the materials of either of the two groups is inclusive of the other groups sensing material.

09/744799

JC02 Rec'd PCT/PTO 30 JAN 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re PCT application of PURDUE RESEARCH FOUNDATION, et al.	) Authorized Officer:) Arlen Soderquist))
International Application Number PCT/US99/17422	)) Facsimile Transmission) Date) December 12, 2000
International Filing Date 30 July 1999	)) Agent's File) Reference:
Title of Invention LOW TEMPERATURE OXYGEN GAS SENSOR	) 7024409PUR93))

RESPONSE TO SECOND WRITTEN OPINION

Assistant Commissioner for Patents
Box PCT
Washington, D.C. 20231

ATTN: IPEA/US

Dear Sir/Madam:

I hereby certify that this correspondence is being facsimile transmitted to the Commissioner of Patents, Washington, D.C. 20231, Facsimile No. (703) 305-3230 on:
~~December 12, 2000~~ December 13, 2000 JBM
(Date of Deposit)
James B. Myers, Jr.
James B. Myers, Jr.
Signature

In response to the Second Written Opinion dated November 14, 2000, Applicants respectfully request consideration of the accompanying remarks.

REMARKS

The Examiner has asserted that claims 1 and 3-7 (as they depend from claim 1) lack novelty under PCT Article 33(3) over Miyahara et al. Applicants respectfully disagree with the Examiner's position. Claim 1 recites that an apparatus comprising an oxygen sensor including a ferroelectric metal oxide sensing member. Applicants submit that for all that Mayahara et al. describes this reference does not disclose or teach a ferroelectric metal oxide sensing member in an oxygen sensor. Consequently, Applicants believe that this rejection is overcome.

The Examiner has also asserted that claims 2 and 3-7 (as they depend from claim 2) lack inventive step under PCT Article 33(3) over Mayahara et al. in view of Vetrone et al., Murayama et al. and Cattan et al. Claim 2 recites an oxygen sensor including a non-stoichiometric metal oxide sensing member having at least two compositional constituents in a ratio that increases along a predetermined direction through said sensing member. Mayahara et al has been discussed above; Applicants also note that Mayahara et al. does not disclose any sensor having at least two compositional constituents whose ratio increases through the sensing member.

Applicants further note that the deficiencies of Mayahara et al. are not corrected by Vetrone et al., Murayama et al. and/or Cattan et al. Only the abstracts of each of these secondary references are provided. None of these abstracts disclose or teach any sensor having at least two compositional constituents whose ratio increases through the sensing member. According, Applicants believe that these rejections are overcome.

Applicants respectfully submits that the captioned International Application meets the criteria of PCT 33(3). Accordingly, Applicants requests further action be taken on this application and the International Preliminary Examination Authority issue a favorable opinion for claims 1-53. Additionally, the Examiner is invited to telephone the undersigned attorney if there are any questions about this submission or other formal matters, which may be addressed in that fashion.

Respectfully submitted

By James B. Myers Jr

James B. Myers, #42,021
Woodard, Emhardt, Naughton,
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Bank One Center/Tower, Suite 3700
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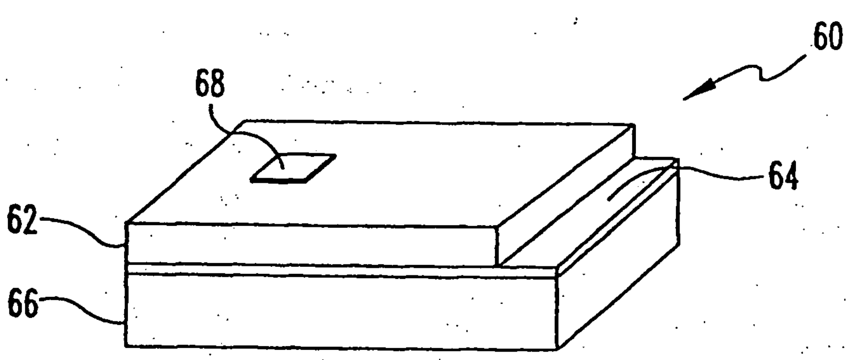
(54) Title: LOW TEMPERATURE OXYGEN GAS SENSOR

(57) Abstract

A highly sensitive oxygen gas sensor (60), which operates at ambient and sub–ambient temperatures was developed using nonstoichiometric metal oxides such as ferroelectric PZT materials or yttria stabilized zirconia. The sensor is constructed of a solid state electrolyte thin film (62) of the nonstoichiometric metal oxide material sandwiched between two metal electrodes (64, 68). An offset d.c. voltage, which is manifested as a translation of the ferroelectric hysteresis loop, develops between the two electrodes (64, 68) when an electric field is applied. The magnitude and direction of the offset voltage depends on variations in oxygen concentration or partial pressure at one of the device electrodes.



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LOW TEMPERATURE OXYGEN GAS SENSOR

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REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Patent Application Nos. 60/094,721 filed on July 30, 1998 and 60/123,819 filed on March 11, 1999, which are both hereby incorporated by reference in their entirety.

BACKGROUND

The present invention relates to sensing devices and the manufacture thereof, and more particularly, but not exclusively, relates to a ferroelectric oxygen gas sensor and a process for manufacturing ferroelectric devices.

Oxygen gas sensors have a wide range of applications in combustion engine and metallurgical processes. The most notable is their use in modern automobile engine operation and control. The sensor measures the oxygen content in the exhaust of the internal combustion engine and adjusts the air-fuel ratio, accordingly. This regulation process has been found to significantly enhance economical operation and environmental control of combustion engines.

Two types of oxygen sensors are commonly used in the auto industry: the potentiometric type, using zirconia based ceramics such as cubic-stabilized zirconia (CSZ) and the resistive type, using titania (TiO_2). A CSZ potentiometer type sensor requires a porous metal electrode and a reference gas at the reference electrode. A high emf develops across the electrodes as the oxygen partial pressure at the sensing electrode varies or changes in comparison to the reference gas at the reference electrode. Furthermore, the sensing mechanism is a thermally activated process, which requires that the sensor be operated at a temperature higher than 300°C in order to register a significant output voltage. This is usually accomplished by positioning the sensor in a hot exhaust gas stream or by heating the sensor using an electric heater. Resistive titania sensors, on the other hand, do not require a reference gas, but do require a tip temperature $\geq$ 350°C for sensor activation. Titania sensors also exhibit strong temperature dependence and require compensation for temperature variations.

Other types of solid-state oxygen sensors using LaF_3 and nonstoichiometric perovskite thin films have recently been reported. Unlike CSZ and TiO_2 sensors, the LaF_3 sensors operate at ambient temperatures, but they suffer from very long response times. Shorter response times of a few minutes were reported by operating the LaF_3 thin films at higher temperatures or by using a special type of a sensitive electroding material such as metal phthalocyanine. Sensing capabilities of non-stoichiometric perovskite thin films only appear to have been reported at higher activation temperatures for sensor activation. Thus, the need to develop a low temperature oxygen sensor with a fast response time remains. Furthermore, a low temperature sensor will have a great advantage in a wide variety of applications including medical (life support), biological and environmental applications and process monitoring.

The present invention meets such needs, and has other benefits and advantages.

SUMMARY OF INVENTION

The present invention relates to sensing devices, the manufacture and use thereof. Various aspects of the invention are novel, nonobvious, and provide various advantages. While the actual nature of the invention covered herein can only be determined with reference to the claims appended hereto, certain forms and features, which are characteristic of the preferred embodiments disclosed herein, are described briefly as follows.

One form of the present includes an oxygen sensor having an operating temperature preferably below about 400K. The temperature is more preferably below about 375K and still more preferably below about 300K. The oxygen sensor includes a nonstoichiometric metal oxide sensor member. Preferably the nonstoichiometric sensing member includes an ionic conductor such as a PZT compound or a yttria stabilized zirconia compound (YSZ).

In another form, the invention includes an oxygen sensor having a graded ferroelectric sensing member. The sensing member may be composed of a $PbZr_xTi_yO_3$ (PZT) compound, where the ratio of x to y varies in accordance with a predetermined compositional gradient through the sensing member, and the sum of x + y is generally about one. For this type of ferroelectric material, preferably x is in a range of about 0.5 to 0.8, and y is in a range of about 0.2 to about 0.5. More preferably, x is in a range of about 0.55 to about 0.75, and y is in a range of about 0.25 to about 0.45. Instead of PZT, other ferroelectric materials may be utilized in accordance with the present invention, such as $(Ba,Sr)TiO_3$ (BST), $BaTiO_3$, lanthanum-modified PZT (PLZT), and strontium bismuth tantalate (SBT) to name a few.

In another form, the present invention includes an oxygen sensor having a non-graded ferroelectric sensing member. The sensing member can be composed of a $PbZr_xTi_yO_3$ (PZT) compound wherein the sum of x and y is generally about one. Preferably, x is in the range of about 0.5 to

about 0.8, and y is in a range of about 0.2 to about 0.5. More preferably, x is in the range of about 0.55 to about 0.75, and y is in the range of about 0.25 to about 0.45. Similar to the graded ferroelectric sensing member above, PZT can be substituted with other ferroelectric materials.

The ferroelectric sensing member can include electrodes formed from any suitable material including, but not limited to platinum, silver, gold, metal phthalocyanine, and metal conductive oxides such as indium-doped tin oxide (ITO) to name a few. The electrodes can be formed using conventional patterning techniques.

Another form of the invention includes an oxygen sensing system. This system may be configured to measure oxygen levels in an intake and/or exhaust stream of a vehicle.

In still another form of the invention, a manufacturing technique includes: (a) providing a source of ferroelectric material having a first region with a first composition and a second region with a second composition different from the first composition; (b) irradiating a portion of the first region and a portion of the second region with a laser beam to release a mixture from the source with a predetermined ratio of the first composition to the second composition; and (c) forming a layer of a sensing matrix corresponding to the ratio. Irradiation of the source may be performed by scanning a predetermined path along the source with the laser beam to generate one or more plumes of the first and second compositions. Moreover, different amounts of the first and second regions may be scanned in this manner to vary the composition of one or more such plumes. Material released from the source may be accumulated in one or more layers to provide a corresponding ferroelectric device.

In a further form, the present invention includes a nonstoichiometric metal oxide sensing member to detect oxygen and a circuit electrically coupled to said sensing member operable to apply an electric field to said sensing member. The sensing member may be comprised of a ferroelectric material such as a PZT or another type of nonstoichiometric metal oxide such as YSZ. The electric field applied to the sensing member

may be of a time varying form, with a peak magnitude of at least about 1 volt per μm.

Still a further form of the present invention includes: providing a nonstoichiometric metal oxide sensing member; applying an electric field to said sensing member; and sensing oxygen with said sensing member. The sensing member may be comprised of a ferroelectric material such as a PZT or another type of nonstoichiometric metal oxide such as YSZ. The electric field applied to the sensing member may be of a time varying form with a peak magnitude of at least about 1 volt per μm.

Accordingly, it is one object of the present invention to provide a low temperature oxygen sensing device.

It is another object of the present invention to provide a ferroelectric device.

It is still another object to provide a technique to manufacture a ferroelectric device.

Further objects, features, forms, aspects, advantages, and benefits of the present invention will become apparent from the description and drawings provided herein.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagram of a vehicle employing one embodiment of an oxygen sensor in an exhaust gas stream sensor system.

Figure 2 is a diagram of a vehicle employing one embodiment of an oxygen sensor in an intake gas stream sensor system.

Figure 3 is a perspective view of a sensing device according to one embodiment of the present invention.

Figure 4 is a diagrammatic illustration of one method for depositing a graded ferroelectric material on a substrate.

Figure 5 is a graphical illustration of an Auger depth profile of relative Zr and Ti concentrations for a down-graded film prepared according to the method depicted in Figure 4.

Figure 6 is a graphical illustration of (200) peaks as a function of 2θ obtained from x-ray diffraction analysis of PZT 55/45, PZT 75/25 and compositionally graded PZT films.

Figure 7 is a schematic of a Sawyer-Tower circuit coupled to an oscilloscope.

Figure 8 is a diagram of an atmosphere and temperature controlled probe station including a specimen stage for analyzing an oxygen sensor prepared according to the method depicted in Figure 4.

Figure 9a is a graphical illustration of the time dependence of the voltage offset for one embodiment of an oxygen sensor having a non-graded ferroelectric film of the present invention.

Figure 9b is a graph plotting voltage offset as a function of an applied sinusoidal driving field for one embodiment of an oxygen sensor having a non-graded ferroelectric film of the present invention.

Figure 10a is a graph plotting voltage offset as a function of oxygen concentration for one embodiment of an oxygen sensor having a non-graded ferroelectric film of the present invention.

Figure 10b is a graph plotting voltage offset as a function of oxygen pressure for one embodiment of an oxygen sensor having a non-graded ferroelectric film of the present invention.

Figure 10c is a graph plotting voltage offset as a function of temperature for one embodiment of an oxygen sensor having a non-graded ferroelectric film of the present invention.

Figure 11a is a graph plotting voltage offset as a series of hysteresis loops as a function of an applied sinusoidal driving field for one embodiment of an oxygen sensor having an up-graded ferroelectric film of the present invention.

Figure 11b is a graph plotting voltage offset as a series of hysteresis loops as a function of an applied sinusoidal driving field for one embodiment of an oxygen sensor having a down-graded ferroelectric film of the present invention.

Figure 12 is a graph plotting voltage offset as a function of the log of oxygen pressure for an oxygen sensor having an up-graded ferroelectric film and an oxygen sensor having a down-graded ferroelectric film, which were prepared in accordance with this invention.

Figure 13 is a graph plotting the voltage offset as a function of temperature for one embodiment of an oxygen sensor having an up-graded film of the present invention.

Figure 14 is a graph plotting voltage offset as a function of Log[pO_2/atm] of a YSZ film prepared according to the present invention.

Figure 15 is a graph plotting voltage offset as a function of the applied sinusoidal driving frequency for a YSZ film prepared according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

For the purpose of promoting an understanding of the principles of the invention, reference will now be made to the embodiments illustrated in the drawings and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended. Any alterations and further modifications in the described device and methods, and any further applications of the principles of the invention as described herein are contemplated as would normally occur to one skilled in the art to which the invention relates.

One embodiment of the present invention is an oxygen sensor having a variety of uses, most notably for use in sensing systems for combustion engines to measure the oxygen levels in an exhaust gas stream and/or an intake gas stream. This oxygen sensor comprises a sensing member made of either a graded or non-graded ferroelectric or other nonstoichiometric metal oxide. At least two electrodes are attached to the sensing member in spaced a part relationship from one another to provide a sensing device akin to a capacitor. When the resulting capacitor device is subjected to an applied electrical driving field, the capacitor exhibits a voltage offset under selected conditions. The magnitude of the voltage offset is dependent upon the gaseous oxygen concentration to which the device is exposed.

Oxygen sensors of the present invention can be used to enhance the efficient operation and environment or pollution control of combustion engines. Figure 1 is a diagram of a vehicle 10 having a combustion engine 12 employing sensing system 14. Sensing system 14 includes oxygen sensor 18 positioned in exhaust line 16 and operably coupled to control circuit 20. Circuit 20 may include a means to provide a driving electric field for application to sensor 18 to generate a voltage offset corresponding to oxygen level. Such driving means are more fully discussed hereinafter in connection with Figure 7. In response to a level of oxygen in exhaust gas flowing through exhaust line 16, oxygen sensor 18 provides an oxygen

signal to control circuit 20. And in response to the oxygen signal input, control circuit 20 generates one or more signals to control or adjust the operation of engine 12, which adjustments can include adjusting the fuel/air mixture into engine 12.

An oxygen sensor prepared as described herein can also be used in the intake gas stream of a vehicle. Figure 2 is a diagram of a vehicle 40 having a combustion engine 42 employing a sensing system 44. Sensing system 44 includes oxygen sensor 46 positioned in air intake line 48. Oxygen sensor 46 is operably coupled to control circuit 50. Circuit 50 may include a means to provide a driving electric field for application to sensor 46 to generate a voltage offset corresponding to oxygen level. Such driving means are more fully discussed hereinafter in connection with Figure 7. In response to a level of oxygen in the intake gas stream flowing through air intake line 48, oxygen sensor 46 provides an oxygen signal to control circuit 50. Control circuit 50 is responsive to one or more inputs and generates an output signal to control or adjust the operation of engine 42.

When used with combustion engines the inventive oxygen sensor responds to small variations in oxygen levels in the monitored gas stream with sufficient time response and sensitivity to enhance the control and operation of the combustion engine. Furthermore, the sensors function in both heated and non-heated environments for effective sensing of oxygen levels. The sensor can function in non-heated environments, for example, in non-heated intake gas streams and in exhaust gas streams upon initial start up of the engine before the exhaust gas becomes heated. Therefore, the sensors can be used to enhance the control and operation of an engine upon initial startup. Control of engines upon initial start provides particular advantages because that is when the engine operates least efficiently and produces the most pollutants.

It will be understood by those skilled in the art that the sensing systems 14 and 44 including a nonstoichiometric metal oxide electrolyte and driving means prepared according to this invention will have a wide variety of applications besides use with combustion engines, for example,

but not restricted to, life support systems, medical (life support), biological and environmental analysis and process monitoring.

Figure 3 depicts one embodiment of a sensor member 60 prepared according to the present invention. Sensor member 60 includes sensing member 62 deposited on an electrode material 64 formed on substrate 66. A top electrode 68 is formed on sensing member 62. It will be understood by those skilled in the art that a plurality of top electrodes 68 can be formed on sensing member 62. A plurality of electrodes 68 can be coupled to a driving means to enhance detection of the offset voltage with sensor 60 as will be discussed further in connection with Figure 7. The material comprising sensing member 62 can be made of a nonstoichiometric metal oxide material that is operable as a solid-state electrolyte positioned between metal electrodes in the form of a capacitor or an electrochemical cell. Sensing member 62 may be in the form of a thin film that can be grown using controllable film deposition techniques, such as a metallo-organic deposition (MOD) spin-on, PVD (i.e., sputtering or pulsed laser deposition (PLD)), chemical vapor deposition (CVD), or MOCVD.

Figure 4 is a diagrammatic illustration of one method for depositing a graded material 80 on a substrate 82 using PLD. Source target 84 is formed of first region 86 and second region 88. First region 86 includes a first material having a first composition, and second region 88 includes a second material having a second composition different from the first composition. Regions 86, 88 meet at interface 87 which is generally positioned at about a 45° angle relative to vertical axis 92 for the illustrated embodiment. Laser 90 rasters laser beam 91 over surface 94 of source target 86 along path 96 in a boustrophedonic pattern as illustrated. As laser beam 91 scans across target 84, it liberates material from the respective region 86, 88 in the form of a plume 97 that is subsequently at least partially deposited on substrate 82 as graded material 80. It should be appreciated that for each generally horizontal scan of laser beam 91 across target 84, a different amount of material is released from region 86 relative to the amount of material released from region 88 for the illustrated

orientation of interface 87. Correspondingly, material 80 is formed of layers that gradually change in composition relative to the ratio of region 86 material to region 88 material. The temperature of material 80 may be maintained at a level sufficient to promote diffusion for a given layer resulting in a generally homogeneous composition for that layer.

In an alternative embodiment, interface 87 may be differently configured to adjust the ratio for a given scan of laser beam 91 thereacross. Further, in other embodiments, the source target 84 may include more than two differently composed regions to be scanned to provide for other types of compositions.

This deposition process was used in one example to deposit a graded ferroelectric sensing film on a Pt-Ti-SiO_2-Si substrate held at 600°C in 300 mTorr of O_2. The film has been found to be highly (111)-oriented, as determined by x-ray diffraction. For this example, the deposition process employed a source with regions 86 and 88 having the ferroelectric composition of $PbZr_{0.75}Ti_{0.25}O_3$, PZT (75/25); and $PbZr_{0.55}Ti_{0.45}O_3$, PZT (55/45), respectively. Regions 86 and 88 were placed adjacent to one another with the interface at a 45° angle to vertical axis 92. A laser beam was then rastered across the target horizontally while its vertical position was incrementally increased after each horizontal scan as shown by path 96. For each horizontal scan that the laser beam contacted the first and second regions of the target 84, either the first or second composition or both were deposited on substrate 82. Initially, a layer of PZT (55/45) was deposited on substrate 82. During the next scan, the laser beam released an amount of PZT (75/25) as well as an amount of PZT (55/45) from the target source. The relative amounts of PZT 75/25 and PZT 55/45 released from the target for each horizontal scan and deposited on the substrate were substantially equivalent to the amount of each region, 86 and 88, scanned by the laser beam. With each successive scan, the amount of PZT (55/45) deposited became less, while the amount of PZT (75/25) deposited became greater, ending with a final layer of PZT (75/25). For

this example, a total of 15 horizontal scans on the target were performed resulting in a film having a thickness of about 0.3 μm.

For convenience, films with Zr/Ti ratios varying from PZT (75/25) at the substrate to PZT (55/45) at the top surface will be referred to as "up-graded" films. Films with the opposite gradient, i.e. with Zr/Ti ratios varying from PZT (55/45) at the substrate to PZT (75/25) at the top surface, will hereafter be referred to as "down-graded" films. Using the method described above both up-graded and down-graded films can be deposited on substrates.

Both graded and non-graded sensors contain electrodes. A first or "bottom" electrode is formed on the substrate with a small section of the substrate is masked off during deposition to allow access to the bottom electrode. A second or top electrode, is formed via photolithography and sputtering or any other patterning techniques according to procedures well known to those skilled in the art. Materials useful as electrodes, including, for example, platinum, silver, gold, metal phthalocyanine and other conductive metal oxides such as indium-doped tin oxides (ITO) can be used to prepare electrodes. In one example, this second electrode was provided in the form of a number of 50 μm x 50 μm platinum pads. For this example, the resulting sensing structure was like that shown in Figure 3 except for the presence of multiple top electrode pads.

In this manner a compositionally graded sensor element can be prepared at a temperature sufficiently low to be suitable for silicon-based substrates. Correspondingly, processing techniques developed for silicon substrates for use in other applications, such as semiconductor microstructures, may be utilized. The method also obviates the need to interdiffuse successively applied layers each having a compositionally different ferroelectric material.

The relative Zr/Ti concentration of the gradient films as a function of depth is determined using a combination of Auger electron spectroscopy and ion milling to construct a depth profile. X-ray diffraction was used to determine crystalline structure and orientation of the films.

Figure 5 shows the results of Auger depth profiling. The resulting plot is the relative concentration of Zr and Ti as a function of depth for a typical down-graded film prepared as described in connection with Figure 4. The depth profile indicates that the deposition method produces smooth, linear composition gradients, either from PZT (75/25) to PZT (55/45), or vice versa. X-ray diffraction measurements are also consistent with the presence of a range of compositions in the films rather than discrete layers of PZT (55/45) and PZT (75/25).

Figure 6 is a plot of the x-ray diffraction measurements of the (200) peak of an up-graded film prepared as described in connection with Figure 4 along with the (200) peaks for non-graded Zr/Ti 55/45 and Zr/Ti 75/25 films. It is known that the positions of the x-ray peaks for PZT shift with composition. This is evidenced by the two distinct peaks from 55/45 at $2\theta = 44.65°$ and 75/25 at $2\theta = 44.15°$. The peak from the graded film, however, is broad and centered at $2\theta = 44.45°$, which is consistent with a film having a range of compositions between PZT (55/45) and PZT (75/25). Naturally, in other embodiments, oxygen sensors in accordance with the present invention may be manufactured using other processes and techniques as would occur to those skilled in the art.

Figure 7 depicts a schematic of a Sawyer-Tower circuit 110 coupled to an oscilloscope 112. Circuit 110 includes an electrical energy source 114 in the form of a variable voltage supply that generates a frequency adjustable time varying voltage, preferably sinusoidal in nature. Circuit 110 includes a nonstoichiometric metal oxide sensor of the present invention such as a ferroelectric PZT or other type, which is schematically represented as sensor capacitor 115 (C_s). Circuit 110 also includes reference capacitor 117 (C_{ref}) in series with capacitor 115. The time varying voltage from source 114 is applied across the series of capacitors 115, 117, providing a corresponding periodic time varying electric field to drive capacitor 115. The electric field has a peak amplitude or magnitude of at least 1 volt per μm. The peak magnitude of the electric field is more preferably in a range of about 1 to about 1000 volts per μm, and still more

preferably is in a range of about 10 to about 100 volts per μm. A most preferred range of the electric field is about 20 to about 50 volts per μm peak to peak amplitude.

A sinusoidal driving electric field applied to sensor capacitor 115 by circuit 110 generates a hysteretic polarization and an offset voltage. The driving voltage (E_{drive}) generated by source 114 is connected to the x-input of oscilloscope 112 while the voltage across the reference capacitor 117 (C_{ref}) is amplified by amplifier 116 and connected to the y-input of oscilloscope 112. In an ideal system the polarization on the sensor capacitor C_s is proportional to the voltage on the reference capacitor (i.e., sample charge, Q, is equal to the reference capacitor charge, Q_{ref}). In graded and non-graded films, however, a voltage develops across the film leading to voltage across the sensor capacitor 115 (C_s) that is equal and opposite to the voltage across the reference capacitor 117 (C_{ref}).

Circuit 110 was utilized to test the response of various PZT materials with non-graded or graded structures to various mixtures of N_2 and O_2 gases. This response was measured as offset voltage vs. time, t. The ambient oxygen partial pressure, $p(O_2)$, was controlled via two mass-flow controllers that determined the ratio of N_2,, (or Ar gas) and O_2 entering the chamber. Each particular gas mixture was allowed to flow through the chamber for one hour, at which point a driving electric field at 1 KHz was applied. The subsequent offset voltage was measured as a function of time. This was done using the following N_2/O_2 ratios: (100/0); (95/5): (90/10); (80/20); (50/50); and (0/100).

Reported measurements were performed using a specimen stage comprised of an atmosphere and temperature controlled probe station to allow voltage measurements at ambient temperature. Figure 8 is a diagram of a atmosphere and temperature controlled probe station 150 including sample stage 152 that is a combination resistive heater and Joule-Thompson refrigerator enclosed within sealed housing 154. Sensor 153 is positioned on sample stage 152. Housing 154 includes inlet ports 156 and 158 and exit ports 160 and 162. Oxygen from source 164 flows

through line 166 into mass flow controller 168 and then through line 170 to inlet port 158 of housing 154. Nitrogen from source 172 flows through line 174 into mass flow controller 176 and then through line 178 into inlet port 156 of housing 154. Exit port 160 is connected to a vacuum pump (not shown), and exit port 162 is connected to a bypass valve (not shown). Probes 180 and 182 connect an oxygen sensor to the power supply of the Sawyer-Tower circuit (not shown) inside probe station 150. The system includes two mass flow controllers, 168 and 176, which regulate the flow of different gases from sources 164 and 172 into station 150. The mass-flow controllers were calibrated using a commercial zirconia oxygen sensor. In one operation mode to allow voltage measurements at ambient pressure, the gases in station 150 flow out exit port 162 through a bypass valve (not shown). In alternative operation modes at reduced pressure, exit port 162 is closed and gases inside station 150 are removed through exit port 160 using a vacuum pump or other vacuum source to provide a partial vacuum in station 150. In yet another operation mode, an oxygen sensor is mounted on a stage 152 that is a combination of a resistive heater and a Joule-Thompson refrigerator. This allows measurements to be performed at temperatures from 77K to 580K.

Figure 9a is a plot of the voltage offset as a function of time for a non-graded ferroelectric film. The time dependence of the voltage offset, $V_{off}(t)$ has the characteristic shape of a capacitor charging up through a resistance. By varying 117 (C_{ref}) and the amplifier 116 in the Sawyer-Tower circuit, it was determined that the time constant, τ, for the time dependence of V_{off} is approximately equal to $C_{ref}R_{in}$= 10 s. Voltage offsets with this type of time dependent behavior measured using the Sawyer-Tower circuit have previously been shown to be a direct result of an equal and opposite voltage that develops on the sample capacitor. Furthermore, the voltage offset develops only when the driving field is applied, the effect is not observed when the applied field is zero. Figure 9b shows the driving field, E_{drive}, dependence of voltage offset, V_{off}. Below a field, E_{min}, V_{off}

increases monotonically with the driving field. Above E_{min}, V_{off} displays a power law dependence on the driving field.

Figure 10a shows the offset voltage as a function of oxygen concentration measured in various combinations of O_2 and N_2 gas at room temperature using a 1 kHz, to 50 V/μm driving field for a non-graded PZT film. A strong dependence of voltage offset on oxygen partial pressure is observed. Figure 10b shows the offset voltage as a function of the oxygen pressure inside the probe station 150 after it was flushed with oxygen gas and pressurized with oxygen at varying absolute pressures. In both cases the magnitude of offset voltage translates to lower d.c. voltage values as the oxygen pressure decreases. The magnitude of V_{off} increases dramatically as the ambient pO_2 is reduced.

Figure 10c shows the voltage offset as a function of temperature. The voltage offset persists over a wide range of temperatures. In preferred embodiments, a non-graded PZT film develops a d.c. voltage offset when subjected to a sinusoidal driving field over a temperature range from about 180K to about 450K for a non-graded PZT film. Correspondingly, the non-graded PZT film for this example has an effective operating range that at least extends between about 180K and about 450K. More preferably for this example, the non-graded PZT film has an effective operating range at least between about 180K and about 400K; and still more preferably between about 180K and about 375K; where effective operating range is understood to mean that the film provides a significant, measurable d.c. voltage offset in response to an applied electric driving field.

In another form, the present invention includes a compositionally graded ferroelectric device prepared according to the method depicted in Figure 4. The compositionally graded ferroelectric devices exhibited similar characteristics under the influence of a periodically time varying driving electric field. The compositionally graded PZT film develops a d.c. voltage offset under the influence of the field. Figure 11a is a graph plotting the d.c. voltage offset observed as a series of hysteresis loops as a function of the applied sinusoidal driving field for an up-graded PZT film. Figure 11b is

a corresponding plot for the down-graded film. The direction of the voltage offset depends on the direction of the gradient with respect to the substrate. For the up-graded film, application of a non-zero driving field provide hysteresis loops that reach an equilibrium offset after a few seconds. The hysteresis loops for the up-graded film translate in a positive d.c. voltage direction while those for the down-graded film translate in a negative d.c. voltage direction when the applied sinusoidal driving field is increased. The hysteresis loops measurements were made using the Sawyer-Tower circuit depicted in Figure 7 using a 1 kHz driving field that was varied from zero to 50 V/μm.

Compositionally graded devices exhibit results similar to those observed for non-graded devices when subjected to various combinations of O_2 and N_2 gas at room temperature and a 1 kHz, 30 V/μm driving field for the up-graded films. Figure 12 shows the relationship between the offset voltage as a function of Log[pO_2/atm] with a driving field of 1 kHz, 35 V/μm at 300K for up-graded and down-graded films. The plot indicates that the magnitude of the voltage offset depends on the ambient oxygen partial pressure. The offset voltage monotonically increased as the oxygen pressure in the chamber increased.

Figure 13 shows the offset voltage as a function of temperature for an up-graded PZT thin film in the temperature range 300K < T < 400K. Offset voltage was observed to monotonically increase as the temperature increased. Furthermore, a significant response was detected at ambient and sub-ambient temperatures. The voltage offset for a graded PZT film persists over a wide range of temperatures. The d.c. voltage offset for a graded PZT film can be observed as low as 400K, or 375K, and even as low as 300K or lower. Thus the graded PZT film may preferably be used for sensing at temperatures below about 400K. More preferably, sensing may be in a range between about 300K and about 400K.

In yet another form, the inventive oxygen sensor includes an oxygen deficient ionic oxide material. One example of an oxygen deficient ionic oxide is yttria stabilized zirconia (YSZ). In one example, the YSZ films

were fabricated using pulsed laser deposition on Pt-Ti-SiO_2-Si substrates held at 600 °C in 50 mTorr of O_2. The YSZ material has the composition of $Y_xZr_{1-x}O_2$, where x is in the range of 0.0 to 0.15. In a preferred form, YSZ film has the composition of $Y_{0.06}Zr_{0.94}O_2$. The YSZ films were prepared to be approximately 0.8 µm thick and preferentially (111)-oriented as determined by x-ray diffraction.

Figure 14 shows the results of the measurement of V_{off} at 300 K in different pO_2 environments with an applied electric field of 19 V/µm at 100 kHz. For atmospheres of Log[pO_2/atm] ~ 0 to -1, a small (~ 0.1 mV) positive voltage offset was observed which decreased with decreasing pO_2. As Log[pO_2/atm] was reduced below ~ - 0.5, an increasingly negative voltage offset was observed with the largest magnitude of ~ -1.4 mV occurring at Log[pO_2/atm] ~ -3, the lowest pO_2 value tested in this example.

Figure 15 is a graph plotting -V_{off} as a function of the driving frequency and shows the frequency response of a typical sample capacitor driven with a 19 V/µm applied field in an atmosphere of Log[pO_2/atm] ~ -3. The maximum response was observed to occur at a driving frequency of approximately 300 kHz. The magnitude of the voltage offset also increased exponentially with the amplitude of the applied electric field.

Correspondingly, the YSZ film can be used at temperatures below about 300K to sense oxygen. The resulting sensor may be quite small, and it requires no reference gas, making it suitable for biomedical applications (among others).

Any publications, patents, or patent applications cited herein are hereby incorporated by reference as if each publication, patent or patent application were set forth in its entirety herein. The citations incorporated by reference include the following:

While the invention has been illustrated and described in detail in the drawings and foregoing description, the same is to be considered as illustrative and not restrictive in character, it being understood that only the preferred embodiment has been shown and described and that all changes and modifications that come within the spirit of the invention are desired to

be protected. Further, any theory of operation, proof, or finding stated herein is meant to further enhance understanding of the present invention and is not intended to make the scope of the present invention dependent upon such theory, proof, or finding.

CLAIMS

What is claimed is:

1. An apparatus comprising an oxygen sensor including a non-stoichiometric metal oxide sensing member having an effective operating temperature below about 400K.

2. The apparatus of claim 1 having an effective operating temperature below about 375K.

3. The apparatus of claim 2 having an effective operating temperature below about 300K.

4. The apparatus of claim 3, wherein said sensor includes at least two metallic electrodes.

5. The apparatus of claim 4, wherein said electrodes are formed from a material selected from platinum, silver, gold, metal phthalocyanine, and conductive metal oxide.

6. The apparatus of any of claims 1-5 and further comprising a circuit electrically coupled to said sensing member operable to apply a time varying electric field to said sensing member.

7. The apparatus of any of claims 1-6, wherein a ratio between two compositional constituents increases along a predetermined direction through said sensing member to provide a corresponding compositional gradient.

8. The apparatus of claim 7, wherein said two compositional constituents are zirconia and titania.

9. The apparatus of claim 7 or 8, wherein said gradient is established by a number of differently composed layers.

10. The apparatus of claim 7-9, wherein x increases along a direction through said sensing member and y decreases along said direction.

11. The apparatus of any of claims 1-10, wherein said sensing member is formed of $PbZr_xTi_yO_3$; where x is in a range of about 0.5 to about 0.8 and y is in a range of about 0.2 to about 0.5.

12. The apparatus of claim 11, wherein x is in a range of about 0.55 to about 0.75 and y is in a range of about 0.25 to about 0.45.

13. The apparatus of any of claims 7-9, wherein said sensing member includes a number of layers each having a different ratio of x to y.

14. The apparatus of any of claims 7-9, wherein x is about 0.55 and y is about 0.45 along a first surface of said sensing member and x is about 0.75 and y is about 0.25 along a second surface of said sensing member opposite said first surface.

15. The apparatus of any of claims 1-3, wherein said sensing member is comprised of an oxygen deficient ionic oxide material.

16. The apparatus of claim 15 wherein the said sensing member is comprised of a YSZ material.

17. A method of use, comprising detecting oxygen in an intake or exhaust stream of a vehicle with the apparatus of any of claims 1-16.

18. A method of manufacture, comprising:

providing a source of ferroelectric material having a first region with a first composition and a second region with a second composition different from the first composition;

irradiating a portion of the first region and a portion of the second region with a laser to release a mixture from the source with a predetermined ratio of the first composition to the second composition; and

forming a layer of a sensing matrix from the mixture, the mixture corresponding to the ratio.

19. The method of claim 18, wherein said source is a solid composed of $PbZr_xTi_yO_3$; where x and y have a first predetermined ratio in the first region and a second predetermined ratio in the second region, the first predetermined ratio being different from the second predetermined ratio.

20. The method of claim 19, wherein x is about 0.75 in the first region and about 0.55 in the second region and y is about 0.25 in the first region and about 0.45 in the second region.

21. The method of any of claims 18-20, wherein the first region is adjacent the second region with an interface oriented at a predetermined position relative to the laser.

22. The method of any of claims 18-21 further comprising performing said irradiating of a number of different portions of the first and second regions to form a graded ferroelectric sensing member.

23. The method of any of claims 18-22, wherein said irradiating includes scanning a predetermined path along the source with the laser.

24. The method of claim 23, wherein said path includes a number of segments each corresponding to a different ratio of the first composition to the second composition.

25. The method of any of claims 18-24, wherein said forming includes depositing the mixture on a substrate.

26. An oxygen sensor formed by the method of any of claims 18-25.

27. A method of manufacture, comprising:

providing a source of ferroelectric material having a first region with a first composition and a second region with a second composition different from the first composition;

generating a number of plumes each having a different ratio of the first composition to the second composition, each of the plumes being formed from different areas of the first and second regions; and

forming a number of layers each corresponding to a different one of the plumes, the layers each having the different ratio of the first composition to the second composition to provide a ferroelectric device with a predetermined compositional gradient.

28. The method of claim 27, wherein the source is a solid composed of $PbZr_xTi_yO_3$; where x and y have a first predetermined ratio in the first region and a second predetermined ratio in the second region, the first predetermined ratio being different from the second predetermined ratio.

29. The method of claim 28, wherein x is about 0.75 in the first region and about 0.55 in the second region and y is about 0.25 in the first region and about 0.45 in the second region.

30. The method of any of claims 27-29, wherein the first region is adjacent the second region with an interface oriented at a predetermined position relative to a device for performing said generating.

31. The method of any of claims 27-30, wherein said generating the plumes includes irradiating a corresponding number of different portions of the first and second regions.

32. The method of any of claims 27-31, wherein said irradiating includes scanning across a predetermined path along the source with a laser.

33. The method of claim 32, wherein said path includes a number of segments each corresponding to a different one of the plumes.

34. The method of any of claims 27-33, wherein said forming includes depositing material from a first one of the plumes on a substrate.

35. An oxygen sensor formed by the method of any of claims 27-34.

36. An apparatus comprising an oxygen sensor including a PZT ferroelectric sensing member.

37. The apparatus of claim 36 wherein said sensing member is comprised of a graded ferroelectric material.

38. The apparatus of claim 36 or 37 wherein the said sensor includes at least two metallic electrodes.

39. The apparatus of claim 38 wherein said electrodes are formed from a material selected from platinum, silver, gold, metal phthalocyanine, and conductive metal oxide.

40. The apparatus of any of claims 36-39 and further comprising a circuit electrically coupled to said sensing member operable to apply a time varying electric field to said sensing member.

41. The apparatus of claim 37, wherein a ratio between two compositional constituents increases along a predetermined direction through said sensing member to provide a corresponding compositional gradient.

42. The apparatus of claim 41, wherein said gradient is established by a number of differently composed layers.

43. The apparatus of claim 41 or 42, wherein said two compositional constituents are zirconia and titania.

44. The apparatus of any of claims 36-43 wherein said sensing member is formed of $PbZr_xTi_yO_3$; wherein x is in a range of about 0.5 to about 0.8 and y is in a range of about 0.2 to about 0.5.

45. The apparatus of claim 44 wherein x is in a range of about 0.55 to about 0.75 and y is in a range of about 0.25 to about 0.45.

46. A method of use, comprising detecting oxygen in an intake or exhaust stream of a vehicle with the apparatus of any of claims 36-45.

47. A combination, comprising:

a nonstoichiometric metal oxide sensing member to detect oxygen; and

a circuit electrically coupled to said sensing member operable to apply a time varying electric field to said sensing member having a peak magnitude of at least about 1 volt per μm.

48. A combination, comprising:

providing a nonstoichiometric metal oxide sensing member;

applying a time varying electric field to said sensing member having a peak magnitude of at least about 1 volt per μm; and

sensing oxygen with said sensing member during said applying.

49. The combination of claim 47 or 48, wherein said peak magnitude is in a range of about 1 volt per μm to about 1000 volts per μm.

50. The combination of claim 49, wherein said peak magnitude is in a range of about 10 volts per μm to about 100 volts per μm.

51. The combination of any of claims 47-50 wherein said sensing member is comprised of a ferroelectric material.

52. The combination of any of claims 47-51, wherein said sensing member is comprised of a PZT material.

53. The combination of any of claims 47-52, wherein the system is operable to detect oxygen concentration at a temperature below about 400K.

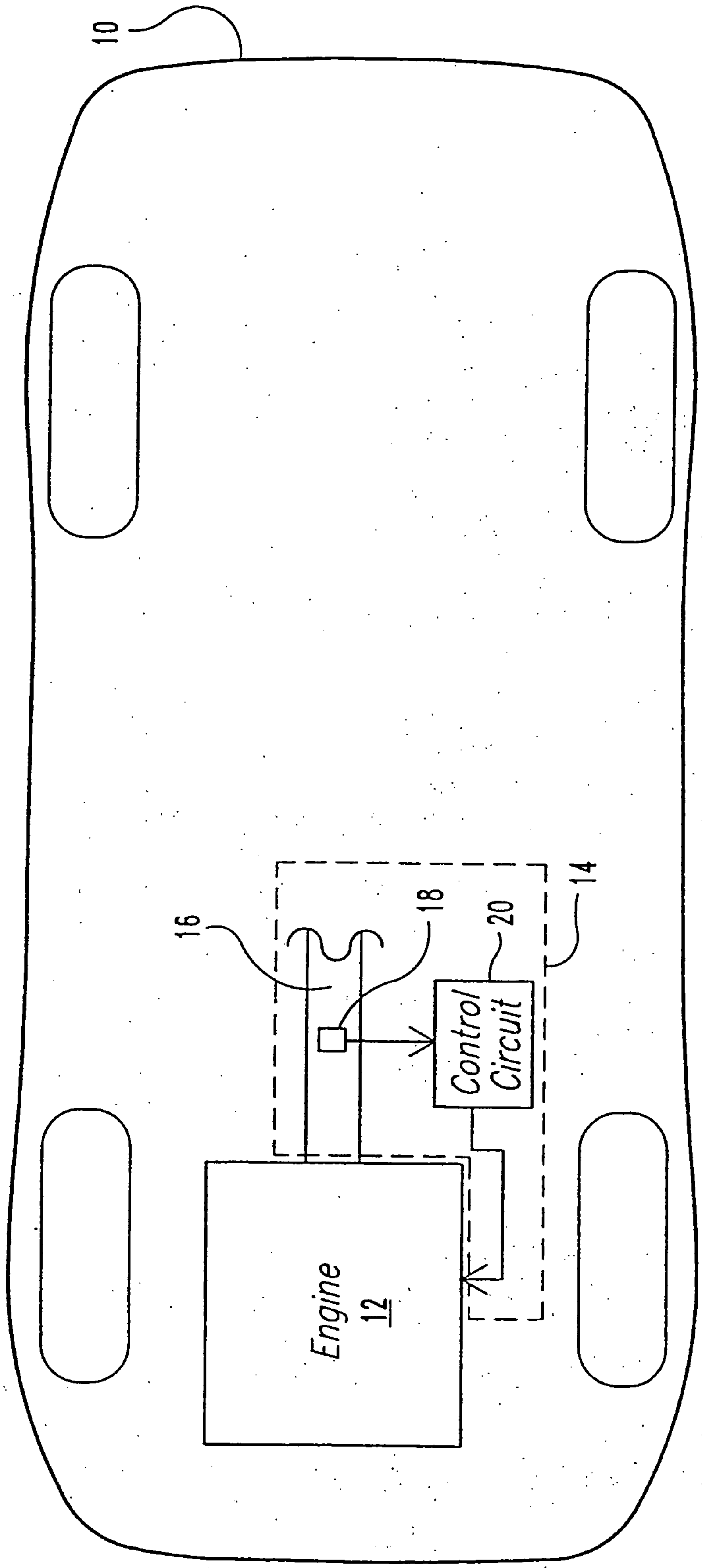

Fig. 1

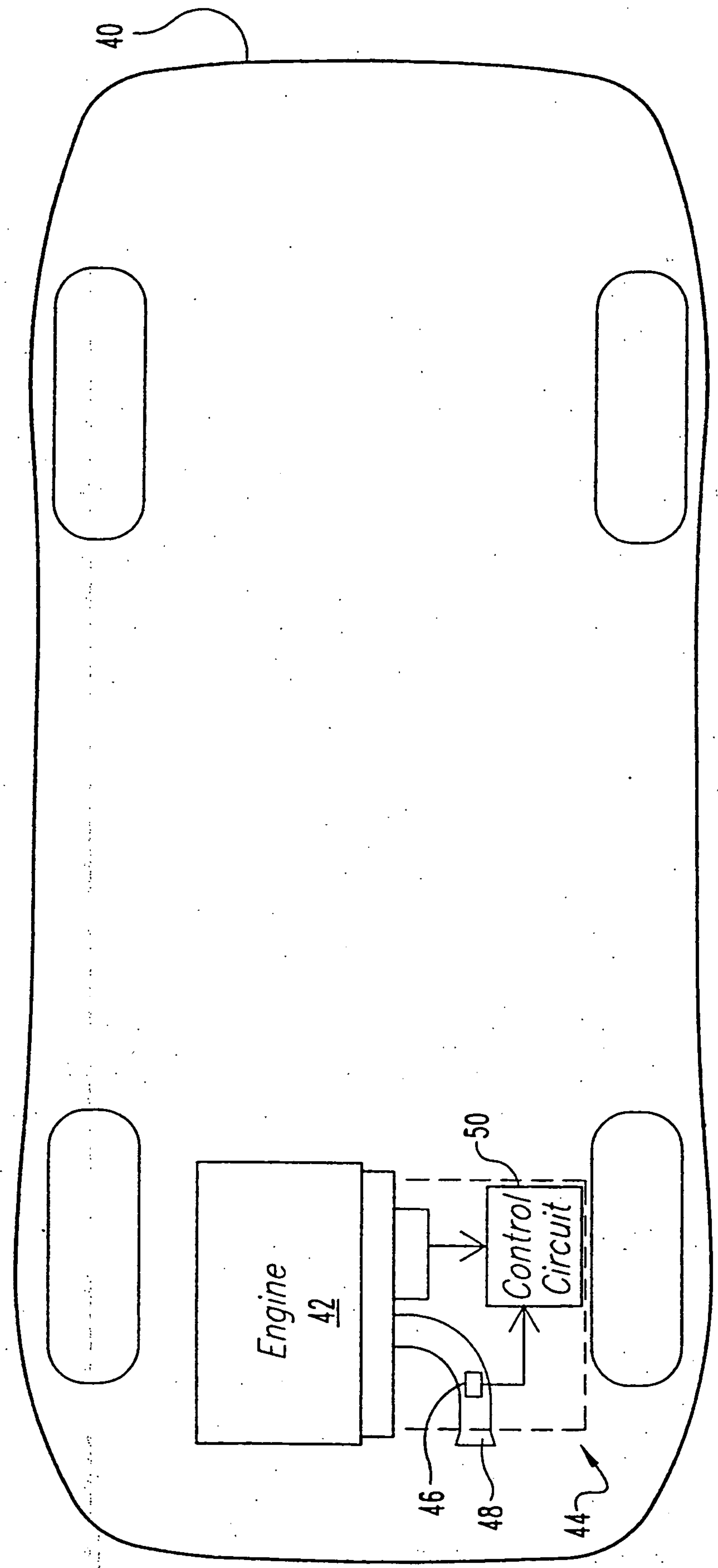

Fig. 2

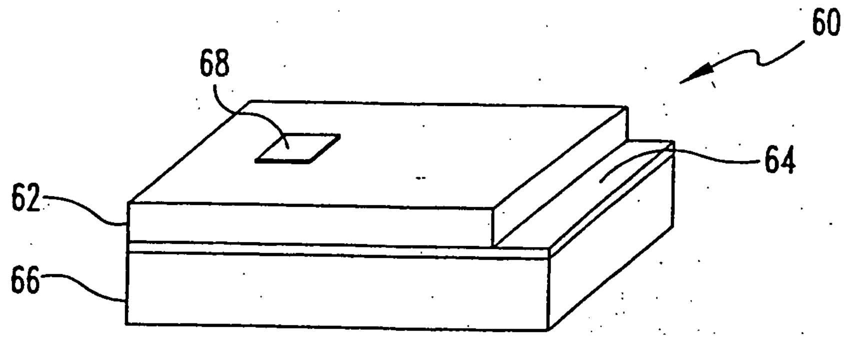

Fig. 3

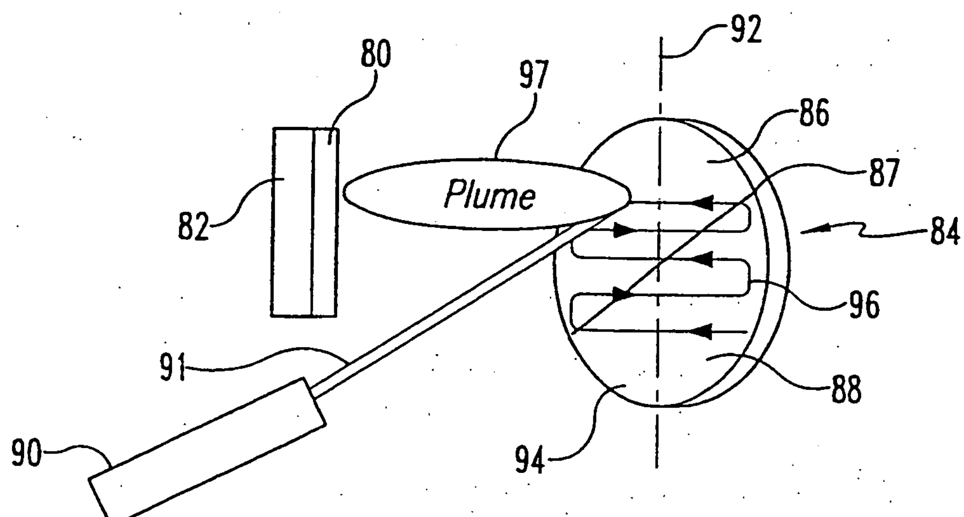

Fig. 4

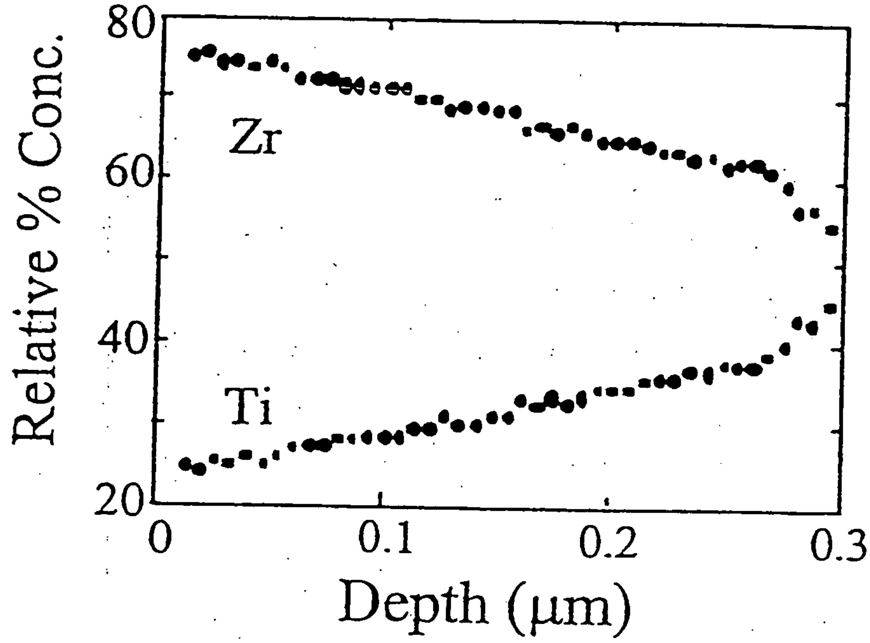
80
60
40
20
Relative % Conc.
Zr
Ti
0
0.1
0.2
0.3
Depth (μm)

Fig. 5

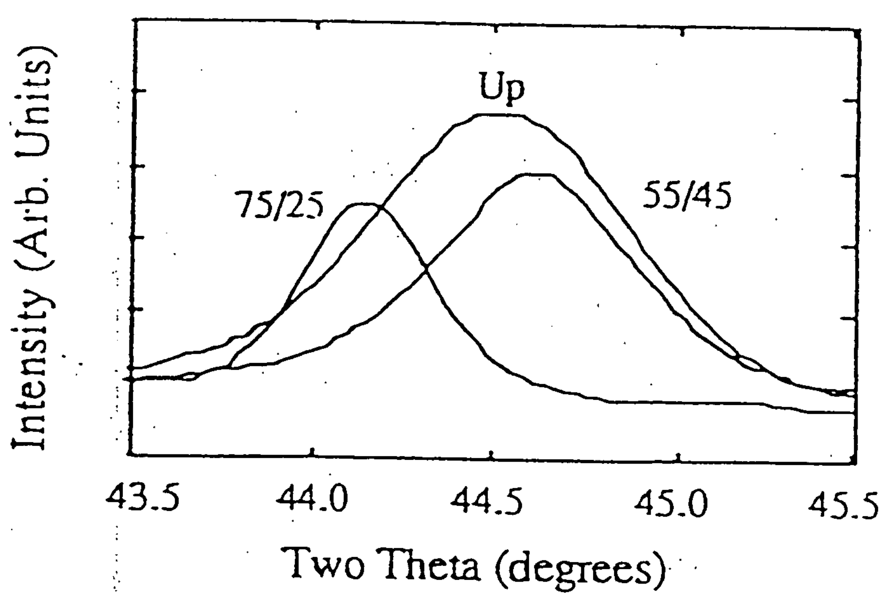
Intensity (Arb. Units)
Up
75/25
55/45
43.5
44.0
44.5
45.0
45.5
Two Theta (degrees)

Fig. 6

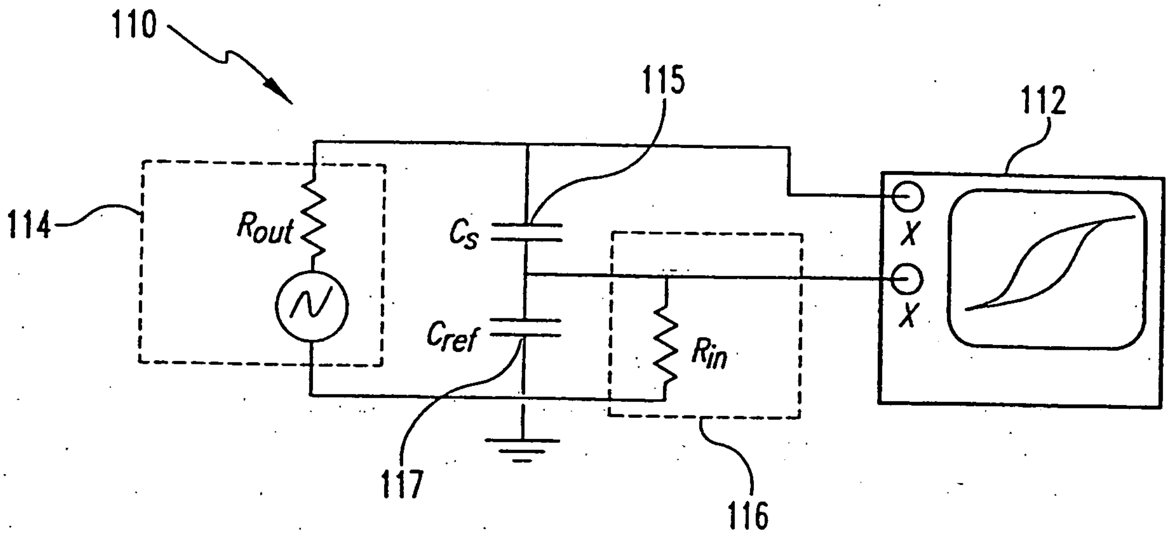
110
115
112
114
R_{out}
C_s
X
X
C_{ref}
R_{in}
117
116

Fig. 7

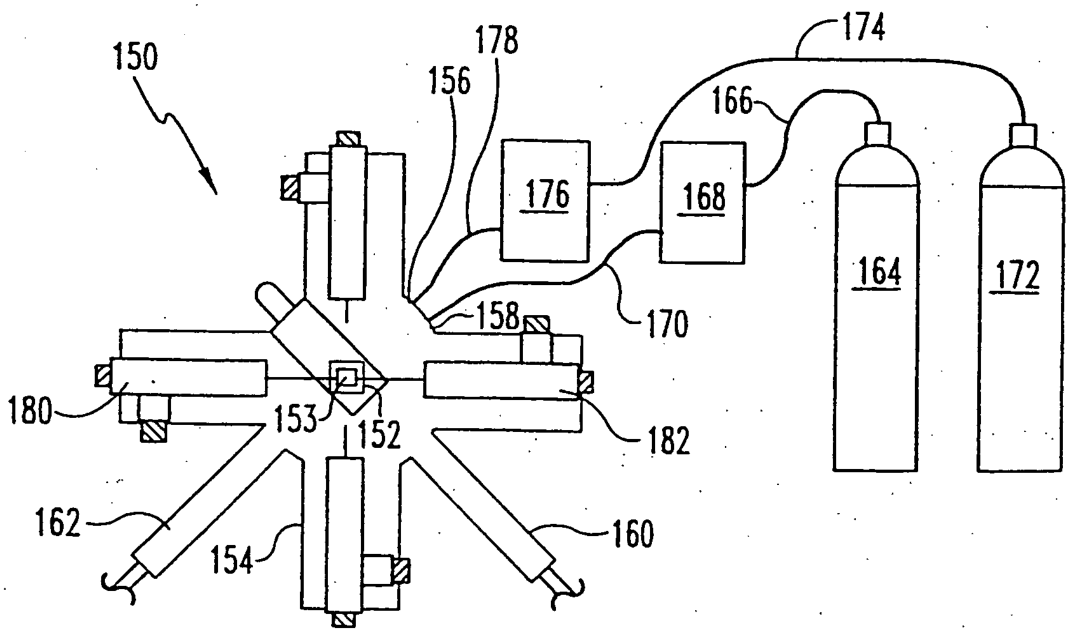
150
156
178
174
166
176
168
164
172
158
170
180
153
152
182
162
154
160

Fig. 8

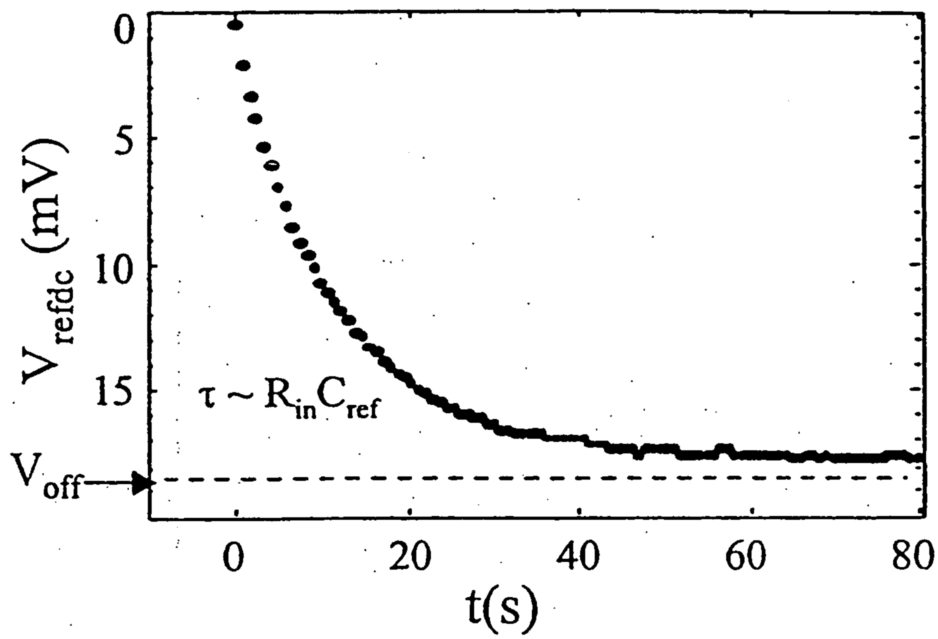
0
5
10
15
V_{refdc} (mV)
$\tau \sim R_{in}C_{ref}$
V_{off}
0
20
40
60
80
t(s)

Fig. 9a

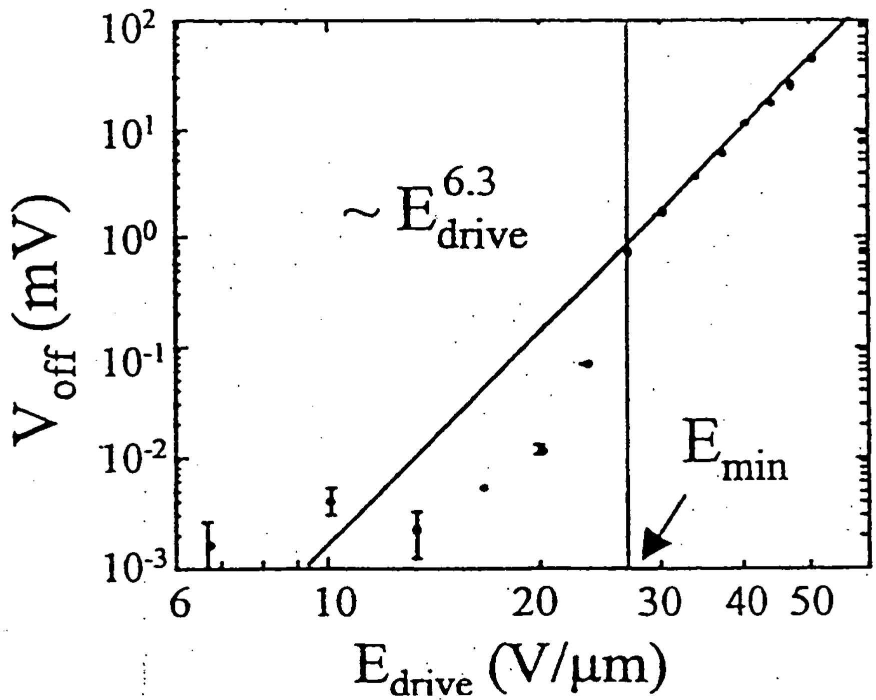
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
V_{off} (mV)
$\sim E_{drive}^{6.3}$
E_{min}
6
10
20
30
40
50
E_{drive} (V/µm)

Fig 9b

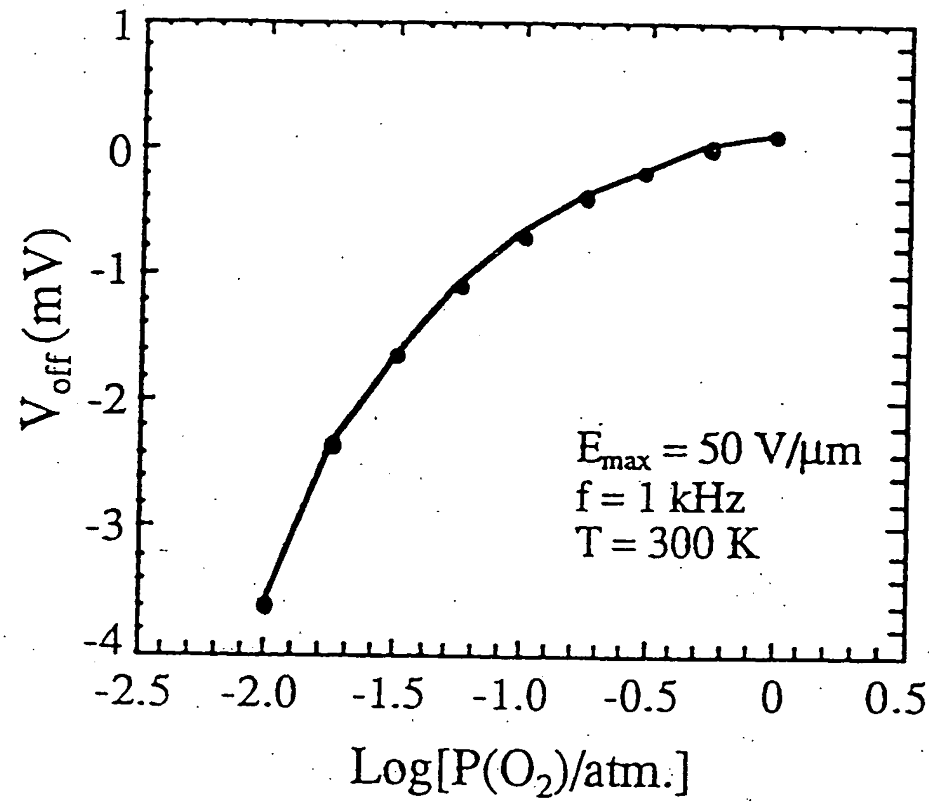

Fig. 10a

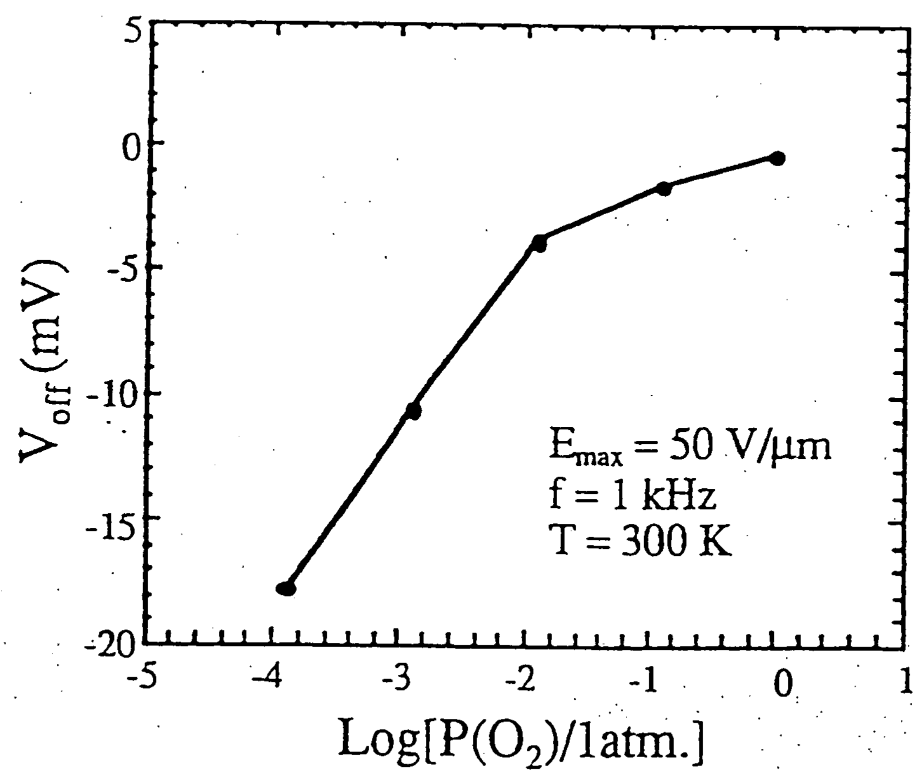

Fig. 10b

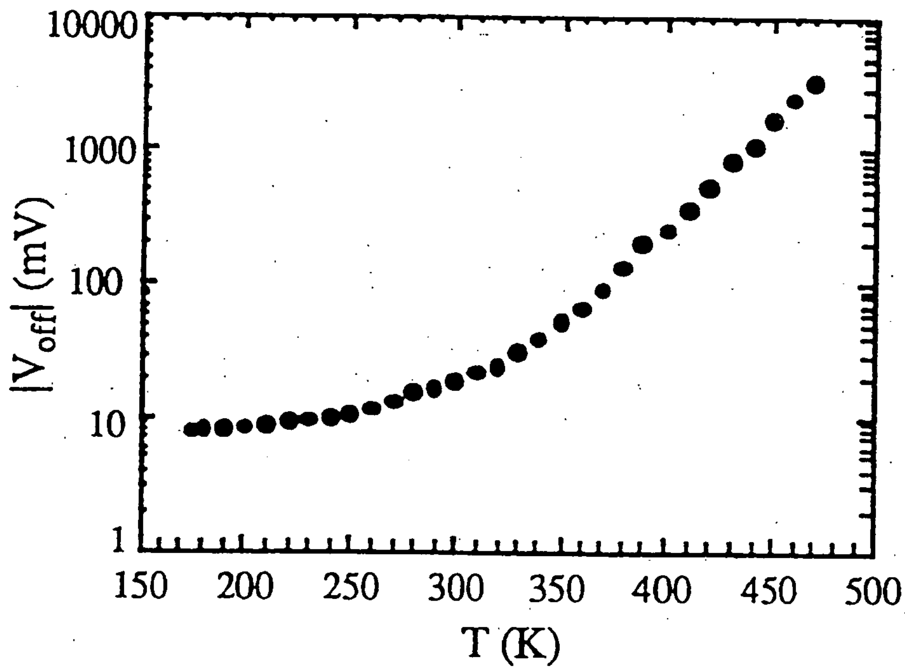

Fig. 10c

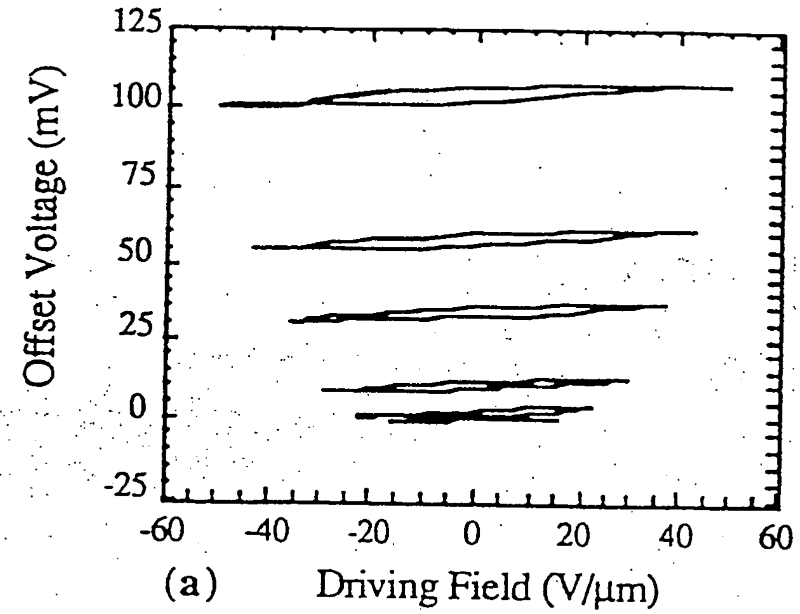

Fig. 11a

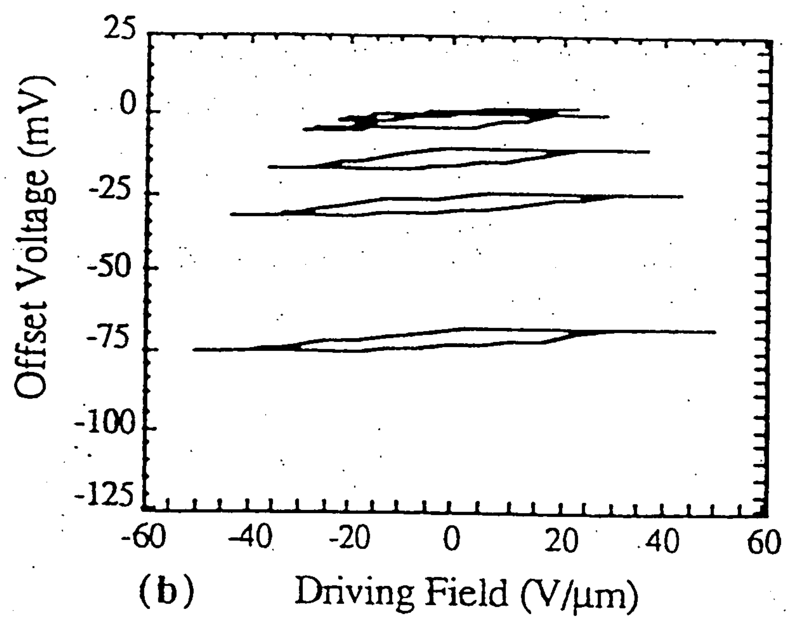

Fig. 11b

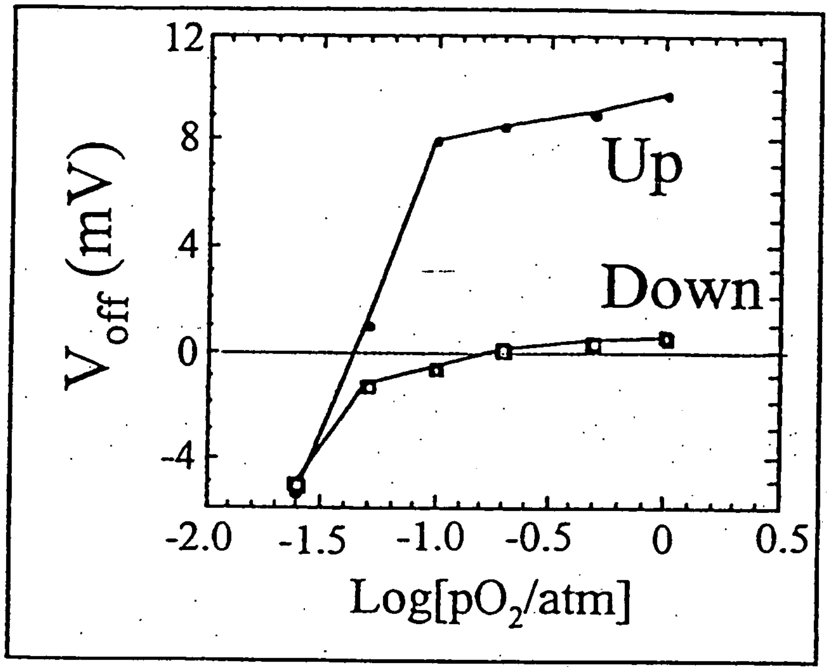
12
8
4
0
-4
V_{off} (mV)
Up
Down
-2.0 -1.5 -1.0 -0.5 0 0.5
Log[pO_2/atm]

Fig. 12

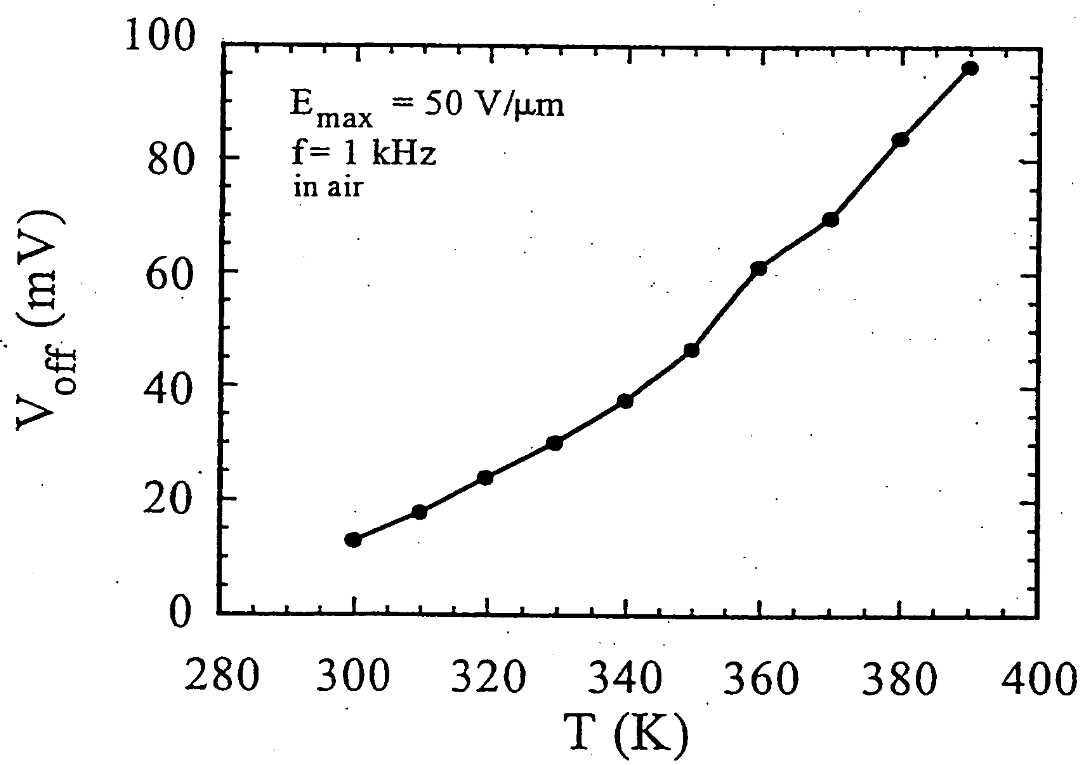
100
80
60
40
20
0
V_{off} (mV)
E_{max} = 50 V/μm
f= 1 kHz
in air
280 300 320 340 360 380 400
T (K)

Fig. 13

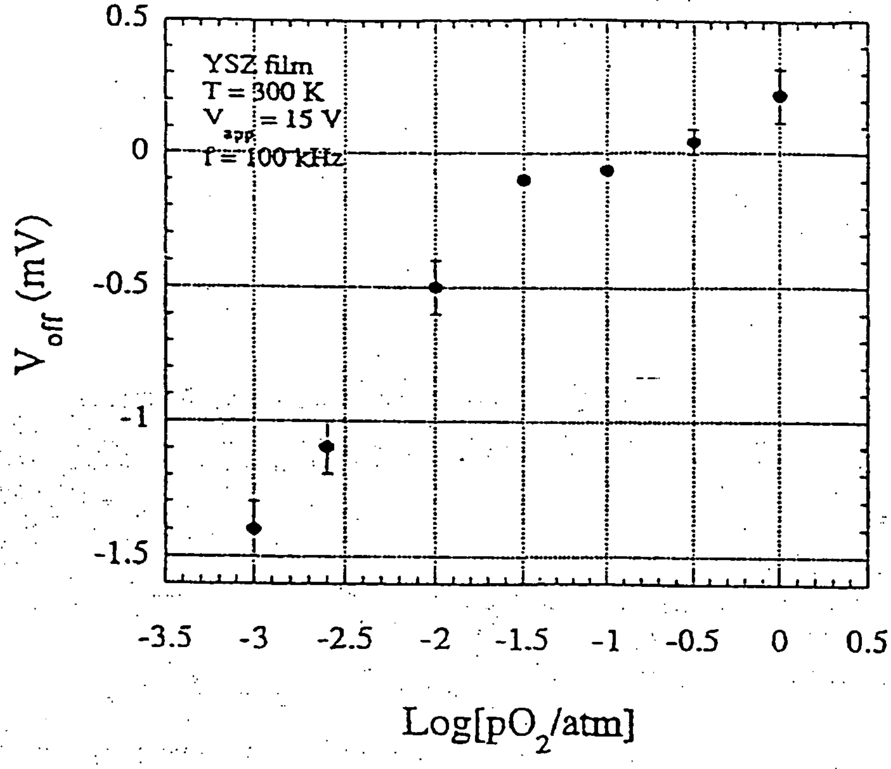
YSZ film
T = 300 K
V_{app} = 15 V
f = 100 kHz
V_{off} (mV)
Log[pO_2/atm]
0.5
0
-0.5
-1
-1.5
-3.5 -3 -2.5 -2 -1.5 -1 -0.5 0 0.5

Fig. 14

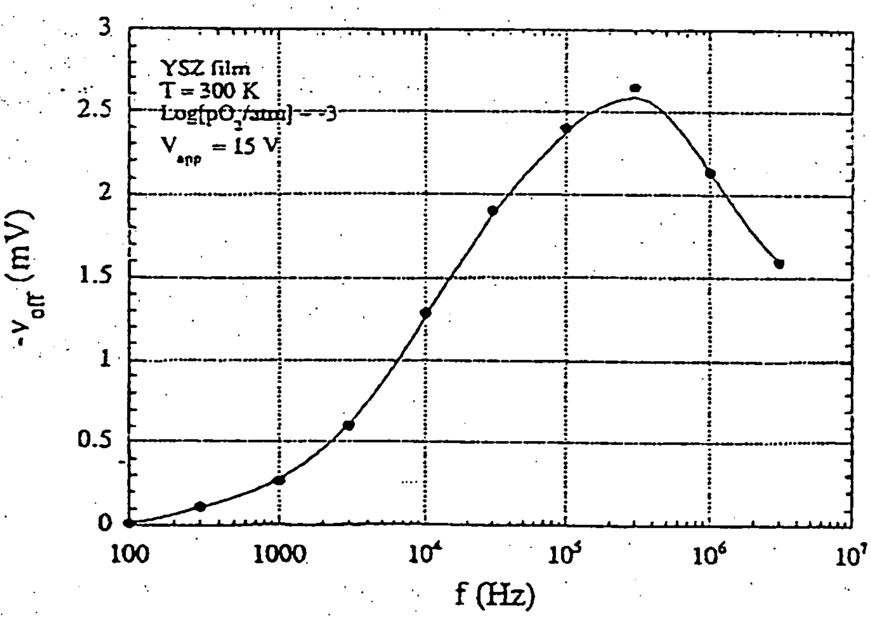
YSZ film
T = 300 K
Log[pO_2/atm] = -3
V_{app} = 15 V
$-V_{off}$ (mV)
f (Hz)
3
2.5
2
1.5
1
0.5
0
100 1000 10^4 10^5 10^6 10^7

Fig. 15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/17422

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :G01N 27/00, 33/00

US CL :73/23.31, 23.32; 422/88, 90, 94, 98; 436/127, 136, 137, 138, 151

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 73/23.31, 23.32; 422/88, 90, 94, 98; 436/127, 136, 137, 138, 151

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	Y. Miyahara et al, "Field-Effect Transistor Using a Solid Electrolyte as a New Oxygen Sensor" J. Appl. Phys., 01 April 1988, Vol. 63, No. 7, pages 2431-2434, see entire document.	1-6,15-16 --------- 36-39,41-43 ,47-50
Y	Chemical Abstracts, Vol. 122, No. 20, 15 May 1995, D.-K. Jang et al, Solid Electrolyte Oxygen Sensor Operating at Low Temperatures" see page 183, column 2, abstract no. 242892x, Sens. Mater., 1995, Vol. 7, No. 1, pages 1-11, see entire document.	1-6,15,16, 36-39,41-43,47-50

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

05 NOVEMBER 1999

Date of mailing of the international search report

30 NOV 1999

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DEBORAH THOMAS
PARALEGAL SPECIALIST

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/17422

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Chemical Abstracts, Vol. 126, No. 1, 06 January 1997, J. Vetrone et al, "Significance of Microstructure for MOCVD-Grown YSZ Thin Film Gas Sensor" see page 1412, column 2, abstract no. 14057f, Mater. Res. Soc. Symp. Proc. 1996, Vol. 403, pages 565-569, see entiore document.	1-6,15,16,36-39,41-43,47-50
Y	Chemical Abstracts, Vol. 129, No. 10, 07 September 1998, G. Petot-Ervas et al, "Electrode Materials, Interface Processes and Transport Properties of Yttria-Doped Zirconia" see page 1125, column 1, abstract no. 128178p, Ionics 1997, Vol. 3, No. 5&6, pages 405-411, see entire document.	1-6,15,16,36-39,41-43,47-50
Y	Chemical Abstracts, Vol. 119, No. 14, 04 October 1993, D. H. Yun et al, "YSZ Oxygen Sensor for Lean Burn Combustion Control System" see page 140, column 2, abstract no. 141710u, Sens. Acuators, B 1993, Vol. 13, No. 1-3, pages 114-116, see entire document.	1-6,15,16,36-39,41-43,47-50
Y	Chemical Abstracts, Vol. 129, No. 24, 14 December 1998, C.-W. Sun et al, "Electrode Resistance of Pt/YSZ Oxygen Sensor and Response Behavior" see page 1528, column 2, abstract 325375b, Wuji Cailiao Xuebao 1998, Vol. 13, No. 4, pages 561-567, see entire document.	1-6,15,16,36-39,41-43,47-50
Y	Chemical Abstracts, Vol. 128, No. 7, 16 February 1998, Y. Murayama et al, "Breath Detection Sensor For Oxygen Delivery System" see page 996, column 2, abstract no. 79966n, Sumitomo Kinzoku Kozan Chuken Shoho 1996, Vol. 11, No. 2, pages 21-26, see entire document.	1-6,15,16,36-39,41-43,47-50
A	P. K. Schenck et al, "Imaging and Gasdynamic Modeling of Pulsed Laser Film Deposition Plumes" Opt. Eng., November 1996, Vol. 35, No. 11, Pages 3199-3205.	1-6,15,16,18-21,27-30,36-39,41-43,47-50
A	D. J. Lichtenwalner et al, "Investigation of the Ablated Flux Characteristics During Pulsed Laser Ablation Deposition of Multicomponent Oxides" J. Appl. Phys. 15 December 1993, Vol. 74, No. 12, pages 7497-7505.	1-6,15,16,18-21,27-30,36-39,41-43,47-50
A	D. P. Vijay et al, "Reactive Ion Etching of Lead Zirconate Titanate (PZT) Thin Film Capacitors" J. Electrochem. Soc., September 1993, Vol. 140, No. 9, pages 2635-2639.	1-6,15,16,18-21,27-30,36-39,41-43,47-50

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/17422

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Chemical Abstracts, Vol. 128, No. 12, 23 March 1998, S. Thiemann et al, "Chemical Modificatons of Au-Electrodes on YSZ and Their Influence on the Non-Nernstian Behavior" see page 770, column 1, abstract no. 142948a, Ionics 1996, Vol. 2, No. 5&6, pages 463-467.	1-6,15,16,18-21,27-30,36-39,41-43,47-50
A	Chemical Abstracts, Vol. 120, No. 2, 10 January 1994, E. Cattan et al, "Physical Properties of Radio-Frequency Magnetron Sputtered Lead(Zirconium,Titanium) Trioxide Thin Films: Direct Determination of Oxygen Composition by Rutherford Backscattering Spectroscopy and Nuclear Reaction Analysis" see page 1945, column 2, abstract no. 22687c, J. Vac. Sci. Technol., A 1993, Vol. 11, No. 5, pages 2808-2815.	1-6,15,16,18-21,27-30,36-39,41-43,47-50
A	N. R. Barnes et al, "Multiband Analysis of Photoluminescence Spectra from Electronically Excited Gas-Phase Species Produced during Laser Ablation of Lead Oxide, Zirconium Oxide, Titanium Oxide, and Lead Zirconate Titanate Targets" Chem. Mater. 1995, Vol. 7, No. 3, pages 477-485.	1-6,15,16,18-21,27-30,36-39,41-43,47-50

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/17422

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 7-14,17,22-26,31-35,40,44-46,51-53
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

STN search in Registry and CA files
search terms: (PB(L)ZR(L)TI(L)O)/ELS, YSZ, DETECTOR?, COUNTER?, SENSOR?, SPECTROG?, SPECTROMET?, PYROMET?, METER#, METRE#, GAUGE?, INDICATOR?, RECORDER?, ANALYZER?, SCANNER?, COMPARATOR?, INSPECTOR?, MONITOR?, DETECT?, SENSE#, SEMSING#, ANALY?, ANAL#, ASSAY?, EST#, ESTN#, ESTIMAT?, QUANTIF?, QUANTITAT?, CALCULAT?, CALC#, CALCN#, MEASUR?, MONITOR?, DETERMIN?, DETERMN#, DET#, DETN#, EVALUAT?, ASCERTAIN?, RECOGNI?, IDENTIF?, INDICAT?, DISTINGUISH?, DIAGNOS?, TEST, TESTS, TESTED, TEST!R?, TESTING#, OXYGEN, YTTRIA#, ZIRCONIA#, STABL?, STABIL?, Y2O3, YTTRIUM# OR DIYTTRIUM#, Y, OXIDE#, TRIOXIDE#, ZRO2, ZIRCONIUM#, ZR, DIOXIDE#, FERROELEC?, FERRO, ELEC#, ELECTRIC?, O, O2

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-6, 15, 16, and 47-50, drawn to apparatus and method including a nonstoichiometric metal oxide sensing member having an effective operating temperature below 400K.
Group II, claim(s) 18-21 and 27-30, drawn to a method of manufacture and an oxygen sensor including a ferroelectric member.
Group III, claim(s) 36-39 and 41-43, drawn to an oxygen sensor and its method of use in which the sensor includes a PZT ferroelectric sensing member.

The inventions listed as Groups I and II or III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: there is no clear connection between the nonstoichiometric sensing material of Group I and the ferroelectric sensing material of either Groups II or III. The sensing materials of Group I while possibly including ferroelectric materials are not so limited. Conversely the sensing materials of Groups II and III also possibly contain nonstoichiometric materials, but are not limited thereto. Additionally Group I has an effective operating temperature limitation that is not found in either of Groups II or III.

The inventions listed as Groups II and III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the sensing material formed through the process of Group II is required to be a mixture of two ferroelectric materials while the ferroelectric sensing material of Group III is limited to a certain type of ferroelectric material. There is no indication that the materials of either of the two groups is inclusive of the other groups sensing material.

PCT/US99/17422

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MAY 01 2000

Woodard, Emhardt, Naughton, Moriarty & McNett

PATENT COOPERATION TREATY

09/744793

From the INTERNATIONAL BUREAU

PCT

To:

PAYNTER, L., Scott
Woodard, Emhardt, Naughton,
Moriarty & McNett
Bank One Center/Tower
Suite 3700
111 Monument Circle
Indianapolis, IN 46204
ETATS-UNIS D'AMERIQUE

INFORMATION CONCERNING ELECTED OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

Date of mailing (day/month/year) 19 April 2000 (19.04.00)		
Applicant's or agent's file reference 7024409PUR93	**IMPORTANT INFORMATION**	
International application No. PCT/US99/17422	International filing date (day/month/year) 30 July 1999 (30.07.99)	Priority date (day/month/year) 30 July 1998 (30.07.98)
Applicant PURDUE RESEARCH FOUNDATION et al		

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

   AP :GH,GM,KE,LS,MW,SD,SL,SZ,UG,ZW
   EP :AT,BE,CH,CY,DE,DK,ES,FI,FR,GB,GR,IE,IT,LU,MC,NL,PT,SE
   National :AU,BG,BR,CA,CN,CZ,DE,IL,JP,KP,KR,MN,NO,NZ,PL,RO,RU,SE,SK,US

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

   EA :AM,AZ,BY,KG,KZ,MD,RU,TJ,TM
   OA :BF,BJ,CF,CG,CI,CM,GA,GN,GW,ML,MR,NE,SN,TD,TG
   National :AE,AL,AM,AT,AZ,BA,BB,BY,CH,CU,DK,EE,ES,FI,GB,GD,GE,GH,GM,HR,HU, ID,IN,IS,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MD,MG,MK,MW,MX,PT,SD,SG,SI,SL,TJ, TM,TR,TT,UA,UG,UZ,VN,YU,ZA,ZW

3. The applicant is reminded that he must enter the "national phase" **before the expiration of 30 months from the priority date** before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing , if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 36(3)(b) and Rule 74.1).

   Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

   The entry into the European regional phase is postponed **until 31 months from the priority date** for all States designated for the purposes of obtaining a European patent.

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No. (41-22) 740.14.35	Authorized officer: F. Baechler Telephone No. (41-22) 338.83.38

Form PCT/IB/332 (September 1997)

3237578

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PATENT COOPERATION TREATY

09 / 744793

M

RECEIVED
APR 04 2000
Woodard, Emhardt, Naughton Moriarty & McNett

To:
L. SCOTT PAYNTER
WOODARD, EMHARDT, NAUGHTON, MORIARTY
&
BANK ONE CENTER/TOWER, SUITE 3700
111 MONUMENT CIRCLE
INDIANAPOLIS, IN 46204

PCT

NOTIFICATION OF RECEIPT OF DEMAND BY COMPETENT INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

(PCT Rules 59.3(e) and 61.1(b), first sentence and Administrative Instructions, Section 601(a))

Date of mailing *(day/month/year)* 30 MAR 2000	
Applicant's or agent's file reference 7024409PUR93	IMPORTANT NOTIFICATION

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US99/17422	30 JUL 99	30 JUL 98

Applicant
PURDUE RESEARCH FOUNDATION

1. The applicant is hereby **notified** that this International Preliminary Examining Authority considers the following date as the date of receipt of the demand for international preliminary examination of the international application:

(29.02.00) 29 Feb 2000

2. That date of receipt is:

- [X] the actual date of receipt of the demand by this Authority (Rule 61.1(b)).
- [ ] the actual date of receipt of the demand on behalf of this Authority (Rule 59.3(e)).
- [ ] the date on which this Authority has, in response to the invitation to correct defects in the demand (Form PCT/IPEA/404), received the required corrections.

3. [ ] **ATTENTION:** That date of receipt is **AFTER** the expiration of 19 months from the priority date. Consequently, the election(s) made in the demand does (do) not have the effect of postponing the entry into the national phase until 30 months from the priority date (or later in some Offices) (Article 39(1)). Therefore, the acts for entry into the national phase must be performed within 20 months from the priority date (or later in some Offices) (Article 22). For details, see the *PCT Applicant's Guide*, Volume II.

   [ ] *(If applicable)* This notification confirms the information given by telephone, facsimile transmission or in person on:

   ____

4. Only where paragraph 3 applies, a copy of this notification has been sent to the International Bureau.

Name and mailing address of the IPEA/	Authorized officer
Assistant Commissioner for Patent Box PCT Washington, D.C. 20231 Attn:RO/US Facsimile No. 703-305-3230	Eric Simms PCT Operations - IAPD Team 1 (703) 305-3761 (703) 305-3230 (FAX) Telephone No.

Form PCT/IPEA/402 (July 1998)

PCT/US99/17422

PATENT COOPERATION TREATY 09 / 744793

RECEIVED

OCT 19 1999

Woodard, Emhardt, Naughton, Moriarty & McNett

PCT

From the INTERNATIONAL BUREAU

To:

PAYNTER, L., Scott
Woodard, Emhardt, Naughton,
Moriarty & McNett
Bank One Center/Tower
Suite 3700
111 Monument Circle
Indianapolis, IN 46204
ÉTATS-UNIS D'AMÉRIQUE

NOTIFICATION CONCERNING SUBMISSION OR TRANSMITTAL OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

Date of mailing (day/month/year) 29 September 1999 (29.09.99)	
Applicant's or agent's file reference 7024409PUR93	**IMPORTANT NOTIFICATION**
International application No. PCT/US99/17422	International filing date (day/month/year) 30 July 1999 (30.07.99)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 30 July 1998 (30.07.98)
Applicant PURDUE RESEARCH FOUNDATION et al	

1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).

2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.

3. An **asterisk(*)** appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

4. The **letters "NR"** appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
30 July 1998 (30.07.98)	60/094,721	US	24 Sept 1999 (24.09.99)
11 Marc 1999 (11.03.99)	60/123,819	US	23 Sept 1999 (23.09.99)

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No. (41-22) 740.14.35	Authorized officer Carlos Naranjo CN Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREATY

09/744793

From the INTERNATIONAL BUREAU

PCT

To:
PAYNTER, L., Scott
Woodard, Emhardt, Naughton,
Moriarty & McNett
Bank One Center/Tower
Suite 3700
111 Monument Circle
Indianapolis, IN 46204
ÉTATS-UNIS D'AMÉRIQUE

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

Date of mailing (day/month/year) 10 February 2000 (10.02.00)		
Applicant's or agent's file reference 7024409PUR93	**IMPORTANT NOTICE**	
International application No. PCT/US99/17422	**International filing date** (day/month/year) 30 July 1999 (30.07.99)	**Priority date** (day/month/year) 30 July 1998 (30.07.98)
Applicant PURDUE RESEARCH FOUNDATION et al		

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
   AU,CN,EP,IL,JP,KP,KR,US

   In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:
   AE,AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CU,CZ,DE,DK,EA,EE,ES,FI,GB,GD,GE,GH,GM,HR,HU,ID,IN,IS,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MD,MG,MK,MN,MW,MX,NO,NZ,OA,PL,PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TR,TT,UA,UG,UZ,VN,YU,ZA,ZW
   The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 10 February 2000 (10.02.00) under No. WO 00/07001

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a **demand for international preliminary examination** must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the **national phase**, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

Th International Bureau of WIPO **34, chemin des Colombettes** **1211 G neva 20, Switzerland**	Authorized officer J. Zahra
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/17422

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :G01N 27/00, 33/00
US CL :73/23.31, 23.32; 422/88, 90, 94, 98; 436/127, 136, 137, 138, 151
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 73/23.31, 23.32; 422/88, 90, 94, 98; 436/127, 136, 137, 138, 151

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	Y. Miyahara et al, "Field-Effect Transistor Using a Solid Electrolyte as a New Oxygen Sensor" J. Appl. Phys., 01 April 1988, Vol. 63, No. 7, pages 2431-2434, see entire document.	1-6,15-16 --------- 36-39,41-43 ,47-50
Y	Chemical Abstracts, Vol. 122, No. 20, 15 May 1995, D.-K. Jang et al, Solid Electrolyte Oxygen Sensor Operating at Low Temperatures" see page 183, column 2, abstract no. 242892x, Sens. Mater., 1995, Vol. 7, No. 1, pages 1-11, see entire document.	1-6,15,16, 36-39,41-43,47-50

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05 NOVEMBER 1999	30 NOV 1999

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	ARLEN SODERQUIST Pat DEBORAH THOMAS PARALEGAL SPECIALIST
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0661

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Chemical Abstracts, Vol. 126, No. 1, 06 January 1997, J. Vetrone et al, "Significance of Microstructure for MOCVD-Grown YSZ Thin Film Gas Sensor" see page 1412, column 2, abstract no. 14057f, Mater. Res. Soc. Symp. Proc. 1996, Vol. 403, pages 565-569, see entiore document.	1-6,15,16,36-39,41-43,47-50
Y	Chemical Abstracts, Vol. 129, No. 10, 07 September 1998, G. Petot-Ervas et al, "Electrode Materials, Interface Processes and Transport Properties of Yttria-Doped Zirconia" see page 1125, column 1, abstract no. 128178p, Ionics 1997, Vol. 3, No. 5&6, pages 405-411, see entire document.	1-6,15,16,3 6-39,41-43,47-50
Y	Chemical Abstracts, Vol. 119, No. 14, 04 October 1993, D. H. Yun et al, "YSZ Oxygen Sensor for Lean Burn Combustion Control System" see page 140, column 2, abstract no. 141710u, Sens. Acuators, B 1993, Vol. 13, No. 1-3, pages 114-116, see entire document.	1-6,15,16,36-39,41-43,47-50
Y	Chemical Abstracts, Vol. 129, No. 24, 14 December 1998, C.-W. Sun et al, "Electrode Resistance of Pt/YSZ Oxygen Sensor and Response Behavior" see page 1528, column 2, abstract 325375b, Wuji Cailiao Xuebao 1998, Vol. 13, No. 4, pages 561-567, see entire document.	1-6,15,16,36-39,41-43,47-50
Y	Chemical Abstracts, Vol. 128, No. 7, 16 February 1998, Y. Murayama et al, "Breath Detection Sensor For Oxygen Delivery System" see page 996, column 2, abstract no. 79966n, Sumitomo Kinzoku Kozan Chuken Shoho 1996, Vol. 11, No. 2, pages 21-26, see entire document.	1-6,15,16,36-39,41-43,47-50
A	P. K. Schenck et al, "Imaging and Gasdynamic Modeling of Pulsed Laser Film Deposition Plumes" Opt. Eng., November 1996, Vol. 35, No. 11, Pages 3199-3205.	1-6,15,16,18-21,27-30,36-39,41-43,47-50
A	D. J. Lichtenwalner et al, "Investigation of the Ablated Flux Characteristics During Pulsed Laser Ablation Deposition of Multicomponent Oxides" J. Appl. Phys. 15 December 1993, Vol. 74, No. 12, pages 7497-7505.	1-6,15,16,1 8-21,27-30,36-39,41-43,47-50
A	D. P. Vijay et al, "Reactive Ion Etching of Lead Zirconate Titanate (PZT) Thin Film Capacitors" J. Electrochem. Soc., September 1993, Vol. 140, No. 9, pages 2635-2639.	1-6,15,16,1 8-21,27-30,36-39,41-43,47-50

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/17422

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Chemical Abstracts, Vol. 128, No. 12, 23 March 1998, S. Thiemann et al, "Chemical Modificatons of Au-Electrodes on YSZ and Their Influence on the Non-Nernstian Behavior" see page 770, column 1, abstract no. 142948a, Ionics 1996, Vol. 2, No. 5&6, pages 463-467.	1-6,15,16,18-21,27-30,36-39,41-43,47-50
A	Chemical Abstracts, Vol. 120, No. 2, 10 January 1994, E. Cattan et al, "Physical Properties of Radio-Frequency Magnetron Sputtered Lead(Zirconium,Titanium) Trioxide Thin Films: Direct Determination of Oxygen Composition by Rutherford Backscattering Spectroscopy and Nuclear Reaction Analysis" see page 1945, column 2, abstract no. 22687c, J. Vac. Sci. Technol., A 1993, Vol. 11, No. 5, pages 2808-2815.	1-6,15,16,18-21,27-30,36-39,41-43,47-50
A	N. R. Barnes et al, "Multiband Analysis of Photoluminescence Spectra from Electronically Excited Gas-Phase Species Produced during Laser Ablation of Lead Oxide, Zirconium Oxide, Titanium Oxide, and Lead Zirconate Titanate Targets" Chem. Mater. 1995, Vol. 7, No. 3, pages 477-485.	1-6,15,16,18-21,27-30,36-39,41-43,47-50

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/17422

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 7-14,17,22-26,31-35,40,44-46,51-53
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

STN search in Registry and CA files
search terms: (PB(L)ZR(L)TI(L)O)/ELS, YSZ, DETECTOR?, COUNTER?, SENSOR?, SPECTROG?, SPECTROMET?, PYROMET?, METER#, METRE#, GAUGE?, INDICATOR?, RECORDER?, ANALYZER?, SCANNER?, COMPARATOR?, INSPECTOR?, MONITOR?, DETECT?, SENSE#, SEMSING#, ANALY?, ANAL#, ASSAY?, EST#, ESTN#, ESTIMAT?, QUANTIF?, QUANTITAT?, CALCULAT?, CALC#, CALCN#, MEASUR?, MONITOR?, DETERMIN?, DETERMN#, DET#, DETN#, EVALUAT?, ASCERTAIN?, RECOGNI?, IDENTIF?, INDICAT?, DISTINGUISH?, DIAGNOS?, TEST, TESTS, TESTED, TEST!R?, TESTING#, OXYGEN, YTTRIA#, ZIRCONIA#, STABL?, STABIL?, Y2O3, YTTRIUM# OR DIYTTRIUM#, Y, OXIDE#, TRIOXIDE#, ZRO2, ZIRCONIUM#, ZR, DIOXIDE#, FERROELEC?, FERRO, ELEC#, ELECTRIC?, O, O2

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-6, 15, 16, and 47-50, drawn to apparatus and method including a nonstoichiometric metal oxide sensing member having an effective operating temperature below 400K.
Group II, claim(s) 18-21 and 27-30, drawn to a method of manufacture and an oxygen sensor including a ferroelectric member.
Group III, claim(s) 36-39 and 41-43, drawn to an oxygen sensor and its method of use in which the sensor includes a PZT ferroelectric sensing member.

The inventions listed as Groups I and II or III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: there is no clear connection between the nonstoichiometric sensing material of Group I and the ferroelectric sensing material of either Groups II or III. The sensing materials of Group I while possibly including ferroelectric materials are not so limited. Conversely the sensing materials of Groups II and III also possibly contain nonstoichiometric materials, but are not limited thereto. Additionally Group I has an effective operating temperature limitation that is not found in either of Groups II or III.

The inventions listed as Groups II and III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the sensing material formed through the process of Group II is required to be a mixture of two ferroelectric materials while the ferroelectric sensing material of Group III is limited to a certain type of ferroelectric material. There is no indication that the materials of either of the two groups is inclusive of the other groups sensing material.

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

14

Applicant's or agent's file reference 7024409PUR93	**FOR FURTHER ACTION** See Notification of Transmittal of Internati nal Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US99/17422	International filing date *(day/month/year)* 30 JULY 1999	Priority date *(day/month/year)* 30 JULY 1998
International Patent Classification (IPC) or national classification and IPC Please See Supplemental Sheet.		
Applicant PERDUE RESEARCH FOUNDATION		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 9 sheets.

   [X] This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 7 sheets.

3. This report contains indications relating to the following items:

   - I [X] Basis of the report
   - II [ ] Priority
   - III [X] Non-establishment of report with regard to novelty, inventive step or industrial applicability
   - IV [X] Lack of unity of invention
   - V [X] Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI [ ] Certain documents cited
   - VII [ ] Certain defects in the international application
   - VIII [X] Certain observations on the international application

Date of submission of the demand 29 FEBRUARY 2000	Date of completion of this report 30 SEPTEMBER 2000
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer ARLEN SODERQUIST DEBORAH THOMAS PARALEGAL SPECIALIST
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0661

Form PCT/IPEA/409 (cover sheet) (July 1998)★

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US99/17422

I. Basis f the report

1. With regard to the **elements** of the international application:*

☐ the international application as originally filed

☒ the description:
pages (See Attached), as originally filed
pages ______, filed with the demand
pages ______, filed with the letter of ______

☒ the claims:
pages (See Attached), as originally filed
pages ______, as amended (together with any statement) under Article 19
pages ______, filed with the demand
pages ______, filed with the letter of ______

☒ the drawings:
pages (See Attached), as originally filed
pages ______, filed with the demand
pages ______, filed with the letter of ______

☒ the sequence listing part of the description:
pages (See Attached), as originally filed
pages ______, filed with the demand
pages ______, filed with the letter of ______

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language ______ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

☐ the language of publication of the international application (under Rule 48.3(b)).

☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/ or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in printed form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ The statement that the information recorded in computer readable form is identical to the writen sequence listing has been furnished.

4. ☒ The amendments have resulted in the cancellation of:

☒ the description, pages NONE
☒ the claims, Nos. NONE
☒ the drawings, sheets/~~fig~~ NONE

5. ☐ This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* *Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

***Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.*

III. Non-establishment of opini n with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non obvious), or to be industrially applicable have not been and will not be examined in respect of:

☐ the entire international application.

☒ claims Nos. 43

because:

☐ the said international application, or the said claim Nos. _ relate to the following subject matter which does not require international preliminary examination *(specify)*.

☒ the description, claims or drawings *(indicate particular elements below)* or said claims Nos. 43 are so unclear that no meaningful opinion could be formed *(specify)*.

Claim 43 is an improper multiple dependent claim.

☐ the claims, or said claims Nos. _ are so inadequately supported by the description that no meaningful opinion could be formed.

☐ no international search report has been established for said claims Nos. _.

2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

☐ the written form has not been furnished or does not comply with the standard.

☐ the computer readable form has not been furnished or does not comply with the standard.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US99/17422

IV. Lack of unity of invention

1. In response to the invitation to restrict or pay additional fees the applicant has:

- [ ] restricted the claims.
- [X] paid additional fees.
- [ ] paid additional fees under protest.
- [ ] neither restricted nor paid additional fees.

2. [ ] This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

- [ ] complied with.
- [X] not complied with for the following reasons:

Please See Supplemental Sheet.

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

- [ ] all parts.
- [X] the parts relating to claims Nos. 1-6,15-16,18-21,27-30,36-39,41-43,47-50.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US99/17422

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. statement

Novelty (N)	Claims	2,7-14,17-42,44-53	YES
	Claims	1,3-7,15-16	NO
Inventive Step (IS)	Claims	18-35	YES
	Claims	1-17,36-42,44-53	NO
Industrial Applicability (IA)	Claims	1-42,44-53	YES
	Claims	NONE	NO

2. citations and explanations (Rule 70.7)

(See Supplemental Sheet.)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US99/17422

VIII. Certain observations n the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claims 26 and 35 are objected to under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 6 because the claims are indefinite for the following reason(s): they lack sufficient structure to allow them to function as a sensor.

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 10

CLASSIFICATION:
The International Patent Classification (IPC) and/or the National classification are as listed below:
IPC(7): G01N 27/00, 33/00 and US Cl.: 73/23.31, 23.32; 422/88, 90, 94, 98; 436/127, 136, 137, 138, 151

I. BASIS OF REPORT:

This report has been drawn on the basis of the description,
page(s) 1-19, as originally filed.
page(s) NONE, filed with the demand.
and additional amendments:
NONE

This report has been drawn on the basis of the claims,
page(s) NONE, as originally filed.
page(s) NONE, as amended under Article 19.
page(s) NONE, filed with the demand.
and additional amendments:
Pages 20-26, filed with the letter of 13 March 2000.

This report has been drawn on the basis of the drawings,
page(s) 1-11, as originally filed.
page(s) NONE, filed with the demand.
and additional amendments:
NONE

This report has been drawn on the basis of the sequence listing part of the description:
page(s) NONE, as originally filed.
pages(s) NONE, filed with the demand.
and additional amendments:
NONE

IV. LACK OF UNITY OF INVENTION:

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2, and 13.3 is not complied with for the following reasons:
As applicant was previously notified this International Preliminary Examining Authority has found plural inventions claimed in the International Application covered by the claims indicated below:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-6, 15, 16, and 47-50, drawn to apparatus and method including a nonstoichiometric metal oxide sensing member having an effective operating temperature below 400K.
Group II, claim(s) 18-21 and 27-30, drawn to a method of manufacture and an oxygen sensor including a ferroelectric member.
Group III, claim(s) 36-39 and 41-43, drawn to an oxygen sensor and its method of use in which the sensor includes a PZT ferroelectric sensing member.

and it considers that the International Application does not comply with the requirements of unity of invention (Rules 13.1, 13.2 and 13.3) for the reasons indicated below:

The inventions listed as Groups I and II or III do not relate to a single inventive concept under PCT Rule 13.1 because, under

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 11

PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: there is no clear connection between the nonstoichiometric sensing material of Group I and the ferroelectric sensing material of either Groups II or III. The sensing materials of Group I while possibly including ferroelectric materials are not so limited. Conversely the sensing materials of Groups II and III also possibly contain nonstoichiometric materials, but are not limited thereto. Additionally Group I has an effective operating temperature limitation that is not found in either of Groups II or III.

The inventions listed as Groups II and III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the sensing material formed through the process of Group II is required to be a mixture of two ferroelectric materials while the ferroelectric sensing material of Group III is limited to a certain type of ferroelectric material. There is no indication that the materials of either of the two groups is inclusive of the other groups sensing material.

V. 2. REASONED STATEMENTS - CITATIONS AND EXPLANATIONS (Continued):

Claims 1, 3-7 (as they depend from claim 1) and 15-16 lack novelty under PCT Article 33(2) as being anticipated by Miyahara et al. In the paper Miyahara teaches a field-effect transistor using a solid electrolyte as a new oxygen sensor. A field-effect transistor (FET) using a solid electrolyte is proposed as a new oxygen sensor. The sensor is fabricated by depositing a thin layer of yttria-stabilized zirconia (YSZ) on a gate insulator of an insulated gate field-effect transistor (IGFET). As an IGFET has an ability to transform impedance, the potential change produced at the interface between the YSZ layer and a platinum gate electrode can be detected stably, even if the impedance of the YSZ is very high. The response of the fabricated sensor showed good reproducibility at 20°. A linear relation between output voltage and logarithmic partial pressure of oxygen was obtained in the range 0.01-1 atmospheres. Sensitivity of the sensor depends on the thickness of the Pt-gate electrode and sputtering conditions of the YSZ layer. Although selectivity to hydrogen and carbon monoxide was not good at room temperature, it could be improved by increasing the operating temperature to 100°. The developed sensor has several advantages including small size, low output impedance, and solid-state construction. It is potentially applicable to medical uses, process control, and automobiles.

Claims 2, 3-7 (as they depend from claim 2), 8-14, 17, 36-42, and 44-53 lack an inventive step under PCT Article 33(3) as being obvious over the prior art as applied in the immediately preceding paragraph and further in view of Vetrone et al. and Murayama et al. Miyahara does not teach other types of materials or specifics related to the structure of the material.

In the abstract Vetrone et al. discusses the significance of microstructure for MOCVD-grown YSZ thin film gas sensor. They report the fabrication and characterization of a low temperature (200°-400°) thin film gas sensor constructed from a MOCVD-grown yttria-stabilized zirconia (YSZ) layer sandwiched between two platinum thin film electrodes. A reproducible gas-sensing response is produced by applying a cyclic voltage which generates voltammograms with gas-specific current peaks and shapes. Growth conditions are optimized for preparing YSZ films having dense microstructures, low leakage currents, and maximum ion conductivities. In particular, the effect of growth temperature on film morphology and texture is discussed and related to the electrical and gas-sensing properties of the thin film sensor device.

In the abstract Murayama et al teach a breath detection sensor for oxygen delivery

Supplemental B x
(To be used when the space in any of the preceding boxes is not sufficient)

C ntinuation of: Boxes I - VIII

system. An inspiration and expiration detection sensor has been developed from remodeling of the air pressure sensor. The sensor element is pyroelectric PZT, which detects temperature change and derives the pressure signal. Air of the breath, therefore, must flow through a heater which is set in front of the sensor element. The device shows remarkably high sensitivity and high reliability. It has been applied to the oxygen delivery system for the dyspneal patient.

It would have been obvious to one of skill in the art to optimize the properties of the Miyahara et al. device according to the teachings of Vetrone et al. because of the ability to control sensor properties as taught by Vetrone et al. It also would have been obvious to use other materials such as the PZT material of Murayama et al. in the Miyahara et al. device because of their known sensitivity to oxygen.

Claims 18-35 meet the criteria set out in PCT Article 33(2)-(4), because the prior art does not teach or fairly suggest the methods of manufacture as claimed with the use of a ferroelectric material with two regions of different composition which are volatilized by irradiating with a laser to form a sensing matrix based on the ratio of the first composition to the second composition in the released materials.

In the paper dated 13 December 2000, applicant argues that there is not a lack of novelty because the Miyahara et al. reference does not teach a ferroelectric metal oxide sensing member. This is not persuasive because claim 15 clearly sets forth that the ferroelectric metal oxide sensing member is a YSZ (yttria stabilized zirconia) material. This is the sensing member of Murayama et al. therefore the claims lack novelty. The additional reference cited to show the lack of an inventive step are not required to make up the argued deficiency of the Miyahara et al. reference and therefore show the lack of an inventive step for the claims to which they have been applied.

-------------------- NEW CITATIONS --------------------
NONE

CLAIMS

What is claimed is:

1. An apparatus comprising an oxygen sensor including a ferroelectric metal oxide sensing member having an effective operating temperature below about 400K.

2. An apparatus comprising an oxygen sensor including a non-stoichiometric metal oxide sensing member having at least two compositional constituents in a ratio that increases along a predetermined direction through said sensing member to provide a corresponding compositional gradient, said non-stoichiometric metal oxide having an effective operating temperature below about 400K.

3. The apparatus of claim 1 or 2 having an effective operating temperature below about 375K.

4. The apparatus of claim 1 or 2 having an effective operating temperature below about 300K.

5. The apparatus of claim 1 or 2, wherein said sensor includes at least two metallic electrodes.

6. The apparatus of claim 5, wherein said electrodes are formed from a material selected from platinum, silver, gold, metal phthalocyanine, and conductive metal oxide.

7. The apparatus of claim 1 or 2 and further comprising a circuit electrically coupled to said sensing member operable to apply a time varying electric field to said sensing member.

8. The apparatus of claim 2, wherein said at least two compositional constituents are zirconia and titania.

9. The apparatus of claim 2 or 8, wherein said gradient is established by a number of differently composed layers.

10. The apparatus of any of claims 1 or 2, wherein said sensing member is formed of $PbZr_xTi_yO_3$; where x is in a range of about 0.5 to about 0.8 and y is in a range of about 0.2 to about 0.5.

11. The apparatus of claim 10, wherein x increases along a direction through said sensing member and y decreases along said direction.

12. The apparatus of claim 11, wherein x is in a range of about 0.55 to about 0.75 and y is in a range of about 0.25 to about 0.45.

13. The apparatus of claim 10, wherein said sensing member includes a number of layers each having a different ratio of x to y.

14. The apparatus of claim 10, wherein x is about 0.55 and y is about 0.45 along a first surface of said sensing member and x is about 0.75 and y is about 0.25 along a second surface of said sensing member opposite said first surface.

15. The apparatus of claim 1 or 2, wherein said sensing member is comprised of an oxygen deficient ionic oxide material.

16. The apparatus of claim 15 wherein the said sensing member is comprised of a YSZ material.

17. A method of use, comprising detecting oxygen in an intake or exhaust stream of a vehicle with the apparatus of claim 1 or 2.

18. A method of manufacture, comprising:

providing a source of f rroelectric material having a first region with a first composition and a second region with a second composition different from the first composition;

irradiating a portion of the first region and a portion of the second region with a laser to release a mixture from the source with a predetermined ratio of the first composition to the second composition; and

forming a layer of a sensing matrix from the mixture, the mixture corresponding to the ratio.

19. The method of claim 18, wherein said source is a solid composed of $PbZr_xTi_yO_3$; where x and y have a first predetermined ratio in the first region and a second predetermined ratio in the second region, the first predetermined ratio being different from the second predetermined ratio.

20. The method of claim 19, wherein x is about 0.75 in the first region and about 0.55 in the second region and y is about 0.25 in the first region and about 0.45 in the second region.

21. The method of claim 18, wherein the first region is adjacent the second region with an interface oriented at a predetermined position relative to the laser.

22. The method of any of claims 18-21 further comprising performing said irradiating of a number of different portions of the first and second regions to form a graded ferroelectric sensing member.

23. The method of any of claims 18-21, wherein said irradiating includes scanning a predetermined path along the source with the laser.

24. The method of claim 23, wherein said path includes a number of segments each corresponding to a different ratio of the first composition to the second composition.

25. The m thod of any of claims 18-21, wherein said forming includes depositing the mixture on a substrate.

26. An oxygen sensor formed by the method of any of claims 18-21.

27. A method of manufacture, comprising:

providing a source of ferroelectric material having a first region with a first composition and a second region with a second composition different from the first composition;

generating a number of plumes each having a different ratio of the first composition to the second composition, each of the plumes being formed from different areas of the first and second regions; and

forming a number of layers each corresponding to a different one of the plumes, the layers each having the different ratio of the first composition to the second composition to provide a ferroelectric device with a predetermined compositional gradient.

28. The method of claim 27, wherein the source is a solid composed of $PbZr_xTi_yO_3$; where x and y have a first predetermined ratio in the first region and a second predetermined ratio in the second region, the first predetermined ratio being different from the second predetermined ratio.

29. The method of claim 28, wherein x is about 0.75 in the first region and about 0.55 in the second region and y is about 0.25 in the first region and about 0.45 in the second region.

30. The method of claim 27, wherein the first region is adjacent the second region with an interface oriented at a predetermined position relative to a device for performing said generating.

31. The method of any of claims 27-30, wh rein said generating the plumes includes irradiating a corresponding number of different portions of the first and second regions.

32. The method of any of claims 27-30, wherein said irradiating includes scanning across a predetermined path along the source with a laser.

33. The method of claim 32, wherein said path includes a number of segments each corresponding to a different one of the plumes.

34. The method of any of claims 27-30, wherein said forming includes depositing material from a first one of the plumes on a substrate.

35. An oxygen sensor formed by the method of any of claims 27-30.

36. An apparatus comprising an oxygen sensor including a PZT ferroelectric sensing member.

37. The apparatus of claim 36 wherein said sensing member is comprised of a graded ferroelectric material.

38. The apparatus of claim 36 wherein the said sensor includes at least two metallic electrodes.

39. The apparatus of claim 38 wherein said electrodes are formed from a material selected from platinum, silver, gold, metal phthalocyanine, and conductive metal oxide.

40. The apparatus of claim 36 and further comprising a circuit electrically coupled to said sensing member operable to apply a time varying electric field to said sensing member.

41. The apparatus of any of claims 36-40, wherein a ratio between two compositional constituents increas s along a predetermined direction through said sensing member to provide a corresponding compositional gradient.

42. The apparatus of claim 41, wherein said gradient is established by a number of differently composed layers.

43. The apparatus of claim 41 or 42, wherein said two compositional constituents are zirconia and titania.

44. The apparatus of any of claims 36-40 wherein said sensing member is formed of $PbZr_xTi_yO_3$; wherein x is in a range of about 0.5 to about 0.8 and y is in a range of about 0.2 to about 0.5.

45. The apparatus of claim 44 wherein x is in a range of about 0.55 to about 0.75 and y is in a range of about 0.25 to about 0.45.

46. A method of use, comprising detecting oxygen in an intake or exhaust stream of a vehicle with the apparatus of any of claims 36-40.

47. A combination, comprising:

a nonstoichiometric metal oxide sensing member to detect oxygen; and

a circuit electrically coupled to said sensing member operable to apply a time varying electric field to said sensing member having a peak magnitude of at least about 1 volt per µm.

48. A combination, comprising:

providing a nonstoichiometric metal oxide sensing member;

applying a time varying electric field to said sensing member having a peak magnitude of at least about 1 volt per µm; and

sensing oxygen with said sensing member during said applying.

49. The combination of claim 47 or 48, wherein said peak magnitude is in a range of about 1 volt per μm to about 1000 volts per μm.

50. The combination of claim 49, wherein said peak magnitude is in a range of about 10 volts per μm to about 100 volts per μm.

51. The combination of claim 47 or 48 wherein said sensing member is comprised of a ferroelectric material.

52. The combination of claim 47 or 48, wherein said sensing member is comprised of a PZT material.

53. The combination of claim 47 or 48, wherein the system is operable to detect oxygen concentration at a temperature below about 400K.